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WATER OXYGEN DEMAND NO. 2

Study Number 21

Report of a Study Conducted by the

ANALYTICAL REFERENCE SERVICE

TRAINING PROGRAM

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Bureau of State Services
Division of Water Supply and Pollution Control

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1965

The ENVIRONMENTAL HEALTH SERIES of reports was established to report the results of scientific and engineering studies of man's environment: The community, whether urban, suburban, or rural, where he lives, works, and plays; the air, water, and earth he uses and re-uses; and the wastes he produces and must dispose of in a way that preserves these natural resources. This SERIES of reports provides for professional users a central source of information on the intramural research activities of Divisions and Centers within the Public Health Service, and on their cooperative activities with State and local agencies, research institutions, and industrial organizations. The general subject area of each report is indicated by the two letters that appear in the publication number; the indicators are

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Public Health Service Publication No. 999-WP-26

FOREWORD

The Analytical Reference Service is conducted by the Training Program of the Robert A. Taft Sanitary Engineering Center for the evaluation of laboratory methods in the environmental field. Cooperative studies by member organizations, through analysis of identical samples and critical review of methodology, provide the mechanism for:

1. Evaluation of analytical procedures, including precision and accuracy, by comparison of the procedures and results reported by participating laboratories.

2. Exchange of information regarding method characteristics.

3. Improvement or replacement of existing methods by development of more accurate procedures and by development of new methodology for determination of new pollutional components.

Samples are designed to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the ARS staff, the membership, and consultants. Notice of each study is sent to the entire membership.

A portion of the study sample with accompanying data forms for reporting numerical values, a critique of the procedures used, comments on modifications, sources of error, difficulties encountered, or other pertinent factors, is then shipped to each of those who expresses a desire to participate. The results and comments of each study are compiled and a report is prepared.

Initially directed toward examination of water, studies now include air, milk, and food. Some studies are periodically repeated, for the advantage of new members, to evaluate new methods or to reevaluate existing methods.

The selection of studies is guided by the responses to questionnaires periodically circulated among the membership which now includes 198 federal, state, and municipal agencies; industries; universities; consulting firms; and foreign agencies.

James P. Sheehy
Director, Training Program

STUDIES ON WHICH REPORTS HAVE BEEN COMPLETED

Water-Minerals	Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium, and potassium. Studies completed in 1956, 1958, and 1961.
Water-Metals	Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc. Studies completed in 1957 and 1962.
Water-Fluoride	Fluoride in the presence and absence of interferences, with and without distillation using a specified procedure. Studies completed in 1958 and 1961.
Water-Radioactivity	Studies completed in 1959, 1961, and 1963. The first two studies were designed to determine gross beta activity, while the third study was concerned with gross beta and strontium-90 activity.
Water-Surfactant	Surfactant in various waters. Studies completed in 1959 and 1963.
Water-Oxygen Demand	Biochemical oxygen demand and chemical oxygen demand study completed in 1960; COD study completed in 1965.
Water-Trace Elements	Arsenic, boron, selenium, and beryllium. Study completed in 1962.
Freshwater Plankton	Evaluation of the precision and accuracy obtainable by the use of various methods of plankton counting and identification. Study completed in 1964.
Air-Inorganics	Chloride, sulfate, fluoride, and nitrate in aqueous solution and on glass fiber Hi-Vol filter mats. Study completed in 1958.
Air-Lead	Filter paper tape impregnated with lead. Study completed in 1961.
Air-Sulfur Dioxide	Determination of sulfur dioxide in air using a specified method. Study completed in 1963.
Milk-DDT Residue	DDT in milk. Study completed in 1962.

PARTICIPANTS IN THIS STUDY

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American Cyanamid Company, Bound Brook, New Jersey
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Delaware Water Pollution Commission
Department of Municipal Laboratories, Hamilton, Ontario, Canada
Department of Water Resources, Durham, North Carolina
Dow Chemical Company, Midland, Michigan
Erie County Laboratory, Buffalo, New York
Florida State Board of Health (Division of Sanitary Engineering, Jacksonville)
Florida State Board of Health (Pensacola)
Florida State Board of Health (Winter Haven)
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HALL Laboratories Division, Calgon Corporation, Pittsburgh, Pennsylvania
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Missouri Department of Public Health and Welfare
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Montana State Board of Health
NALCO Chemical Company, Chicago, Illinois
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Nevada State Department of Health
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New York State Conservation Department

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U.S. Army Environmental Hygiene Agency, Edgewood Arsenal, Maryland
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University of Beograd, Civil Engineering Faculty, Beograd, Yugoslavia
University of Kansas, School of Engineering and Architecture
University of Leeds, Houldsworth School of Applied Science, Leeds, England
University of North Carolina, Chapel Hill
Virginia State Water Control Board
Washington State Department of Health
Washington State University, Division of Industrial Research
Water Department, Charlotte, North Carolina
Water Department, Long Beach, California
Water Research Association, Marlow, Buckinghamshire, England
West Virginia State Water Resources Commission
Wisconsin State Board of Health

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ABSTRACT

This study consisted of four samples which 74 participating laboratories were instructed to dilute to a specified volume and analyze by both the Standard Method for Chemical Oxygen Demand and by the Mercuric Sulfate modification.

The results from this study indicate that the two procedures produce similar precision and accuracy when no interfering materials are present. When interferences due to high concentrations of chloride are present, the standard method will produce equal precision and accuracy only if the appropriate corrective techniques are applied.

The Mercuric Sulfate modification is the method of choice for COD measurement since with less manipulation it effectively removes the interference due to chloride oxidation and is less time consuming.

WATER-OXYGEN DEMAND NUMBER 2

PURPOSE OF THE STUDY

The chemical oxygen demand (COD) of a liquid sample is one of the oldest analytical parameters of pollution and is used quite frequently. Many oxidants and variations in procedure have been used in the past, but the dichromate procedure, as described in the 11th edition of Standard Methods for the Examination of Water and Wastewater,[1] is used by most analysts today.

A brief evaluation of the precision and accuracy of this test was made in the previous Water-Oxygen Demand study, which involved a sample containing no interfering material and having an oxidizability that varied slightly from the theoretical.

It is generally recognized that chloride ions in the sample prevent a true measurement of the COD. Several remedial measures involving a mathematical correction, either alone or in conjunction with the use of silver sulfate, are offered in Standard Methods. On the other hand, the mercuric sulfate modification developed by Dobbs and Williams,[2] of the Robert A. Taft Sanitary Engineering Center, seemed to remove effectively interference by chlorides. A comparative evaluation of the two methods, therefore, appeared timely.

DESIGN OF THE STUDY

To achieve a sound evaluation of accuracy, a search was undertaken for an oxidizable material that would consistently exert a COD that is 100 % of the theoretical and that would be stable for several months. Potassium acid phthalate was found to meet these requirements in the concentrations used for the samples as shipped.

The study consisted of four samples, designated as A, B, C, and D, which the recipient was instructed to dilute to a specified volume and analyze in triplicate by both the standard method and the mercuric sulfate modification. Instructions for the latter procedure were supplied to the participants.

> Sample A, designed as a control, contained 8.5020 g/liter potassium acid phthalate in sterile distilled water with no interference added. When 10 ml of this sample was diluted to 500 ml, the resulting solution produced a COD of 200 mg/liter.
>
> Sample B, designed to simulate a fairly average sample, contained 6.8016 g/liter potassium acid phthalate and 8.2440 g/liter sodium chloride. When 10 ml of this sample was diluted to 500 ml,

the resulting solution had a COD of 160 mg/liter and a chloride concentration of 100 mg/liter.

Sample C, represented the type of sample most likely to cause erroneous COD values. This sample contained 6.3764 g/liter potassium acid phthalate and 82.4400 g/liter sodium chloride. When 10 ml of this sample was diluted to 500 ml, the theoretical COD of the resulting solution was 150 mg/liter and the chloride content was 1,000 mg/liter.

Sample D was designed to evaluate the overall efficiency of the methods in analyzing a variety of substrates. This sample contained 3.4008 g/liter potassium acid phthalate, and 5 ml was to be diluted to 500 ml with surface water or wastewater (Solution D_1) collected by the participants. The resulting solution (D_2) would then contain 40 mg/liter COD in addition to the COD of the diluent (D_1).

Many participants provided additional analytical data on the water used as Sample D_1.

TREATMENT OF DATA

The mean of the results reported by each participant was plotted on probability paper to determine the distribution. Values showing a deviation from the normal distribution line were rejected as non-representative because of errors in calculation, dilution, or other indeterminate factors. The rejected values are circled on the probability plot. These rejected values were not included in the development of statistical parameters. In several instances in which a mathematical error was noted, the corrected values were submitted in the interim report to the participant for his approval. If the corrected values were approved by the participant, they were then used in the report.

Calculation of the standard deviations was based on the difference between the average result submitted by each participant and the overall mean value reported for each method. The average reported values are also used in the bar charts.

The results obtained by use of the standard method were grouped according to the method employed for correction of chloride interference and are identified as follows:

Technique (1) Mathematical correction
Technique (2) Silver sulfate added before reflux
Technique (3) Silver sulfate added after 20 minutes boiling
Technique (4) Silver sulfate dissolved in the sulfuric acid

Statistical terms, as used in this report, are defined in the glossary.

DISCUSSION

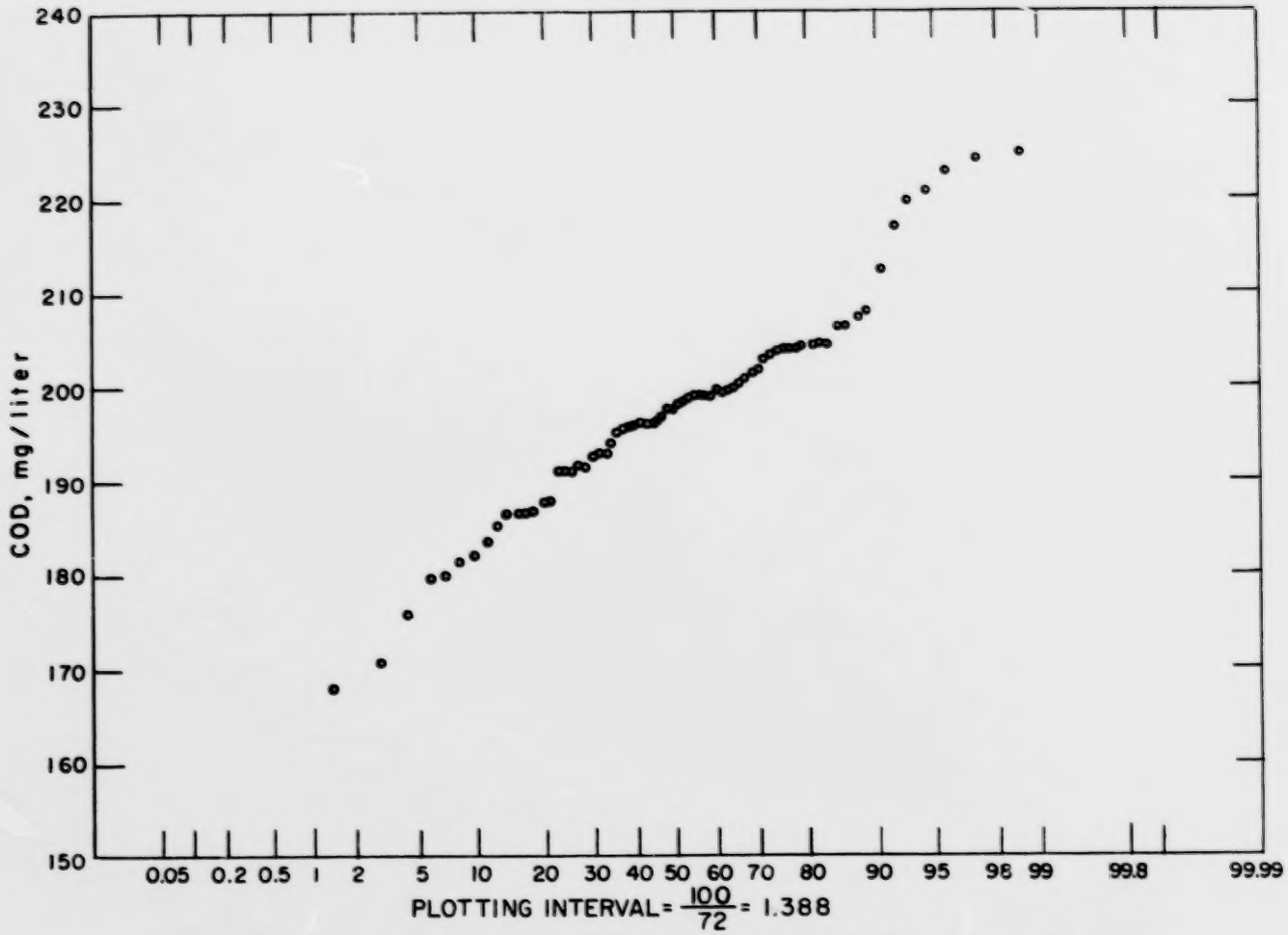
SAMPLE A (200 mg/liter COD in distilled water)

Sample A provided for evaluation of the precision and accuracy of the two methods on waters containing no interfering substances. This sample functioned as a control, and the two methods were expected to produce results of equal accuracy and precision.

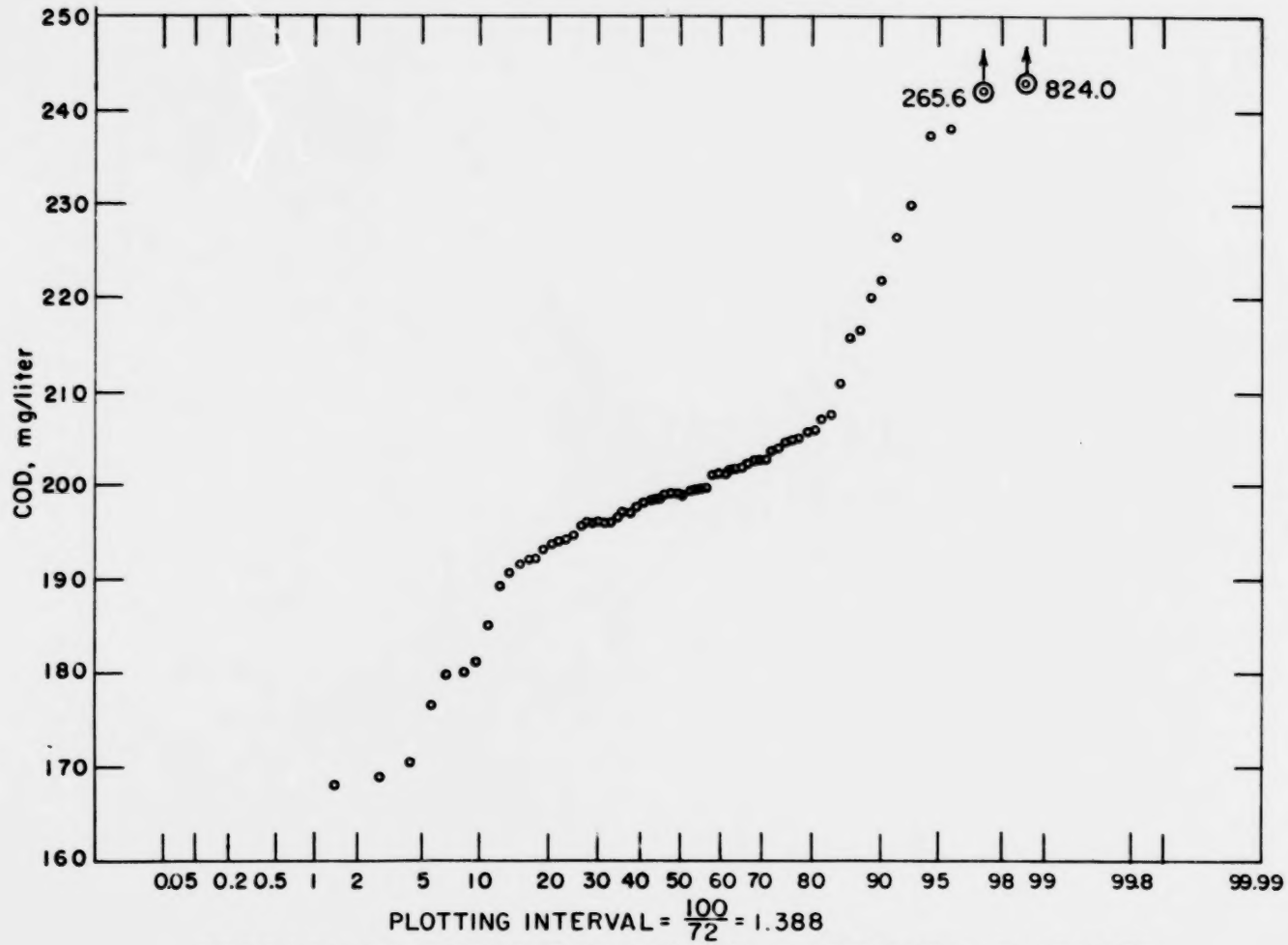
The mercuric sulfate method seems to exhibit slightly more accuracy and a little less precision (Table 1) than the standard method, when the technique for chloride correction is not considered. (See accuracy and precision in Glossary.) The laboratories that used the silver sulfate correction (technique 2) seemed, according to the mean, to achieve better accuracy than those using the other techniques, but the precision was adversely affected. Also, the 50 % range shows that the mean is misleading, since the better half of the results were still twice as far from the theoretical as the results obtained by the other chloride correction techniques. The best standard method values were obtained by the combination of techniques 1 and 3, although no chloride interference was present. Thus, this sample provided an evaluation of procedures rather than efficiency of chloride tie-up. In general, the results indicate that there is very little difference between the two methods when applied to this type of sample.

Table 1. SUMMARY OF STATISTICAL DATA ON SAMPLE A

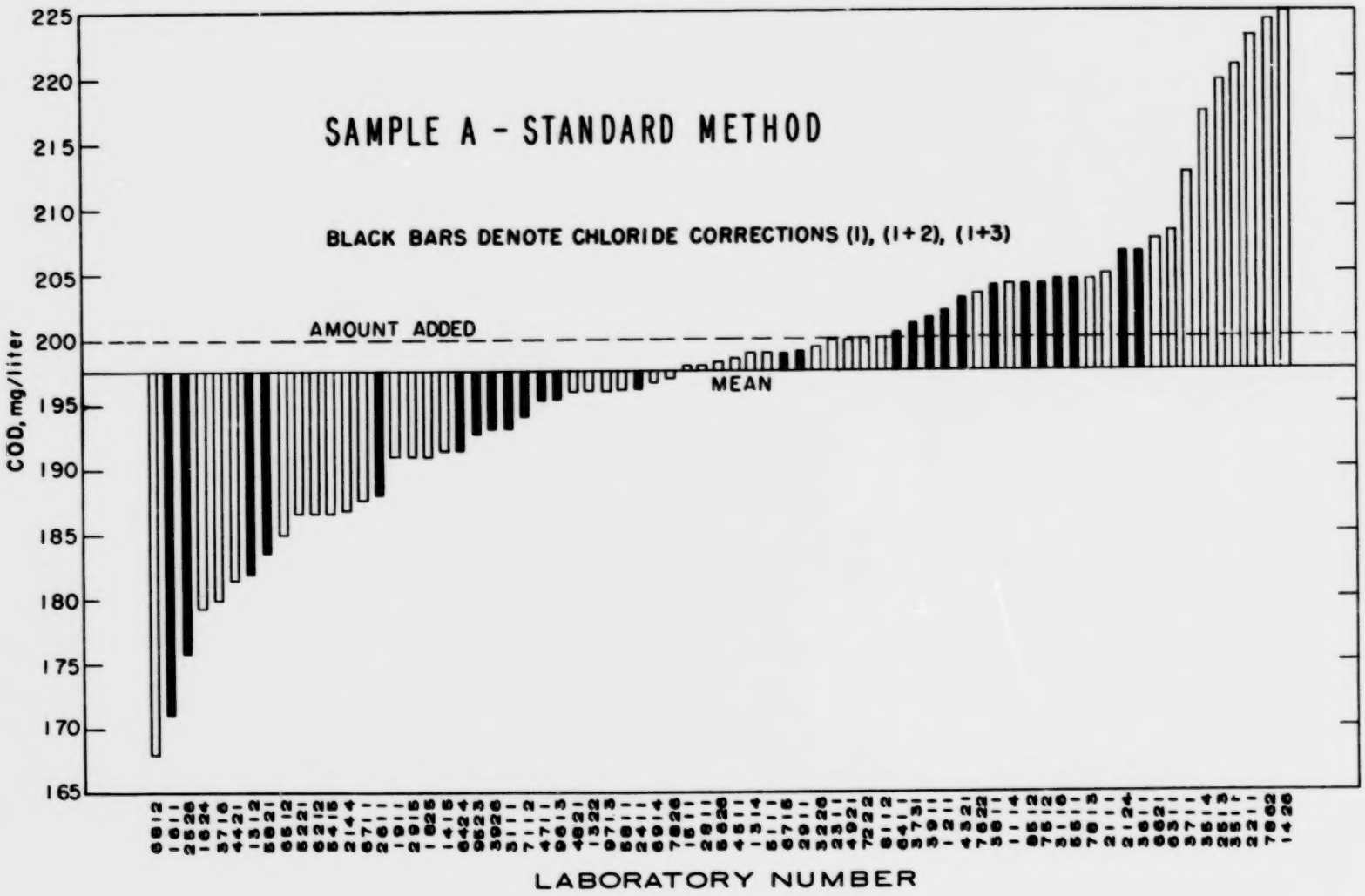
Method	Mean	Standard deviation	Median	50 % range	Number
Mercuric sulfate	200.2	13.1	198.9	± 4.6	69
Standard method, Overall	197.5	11.4	198.2	± 4.8	71
Standard method (1)	194.9	9.2	195.3	± 4.8	15
Standard method (2)	199.8	14.4	199.2	± 8.6	27
Standard method (3)	190.0	13.2	196.8	± 3.2	5
Standard method (4)	194.9	5.8	198.4	± 1.6	5
Standard method (1 + 2)	200.2	----	-----	-----	2
Standard method (1 + 3)	196.0	10.5	200.4	± 4.4	9



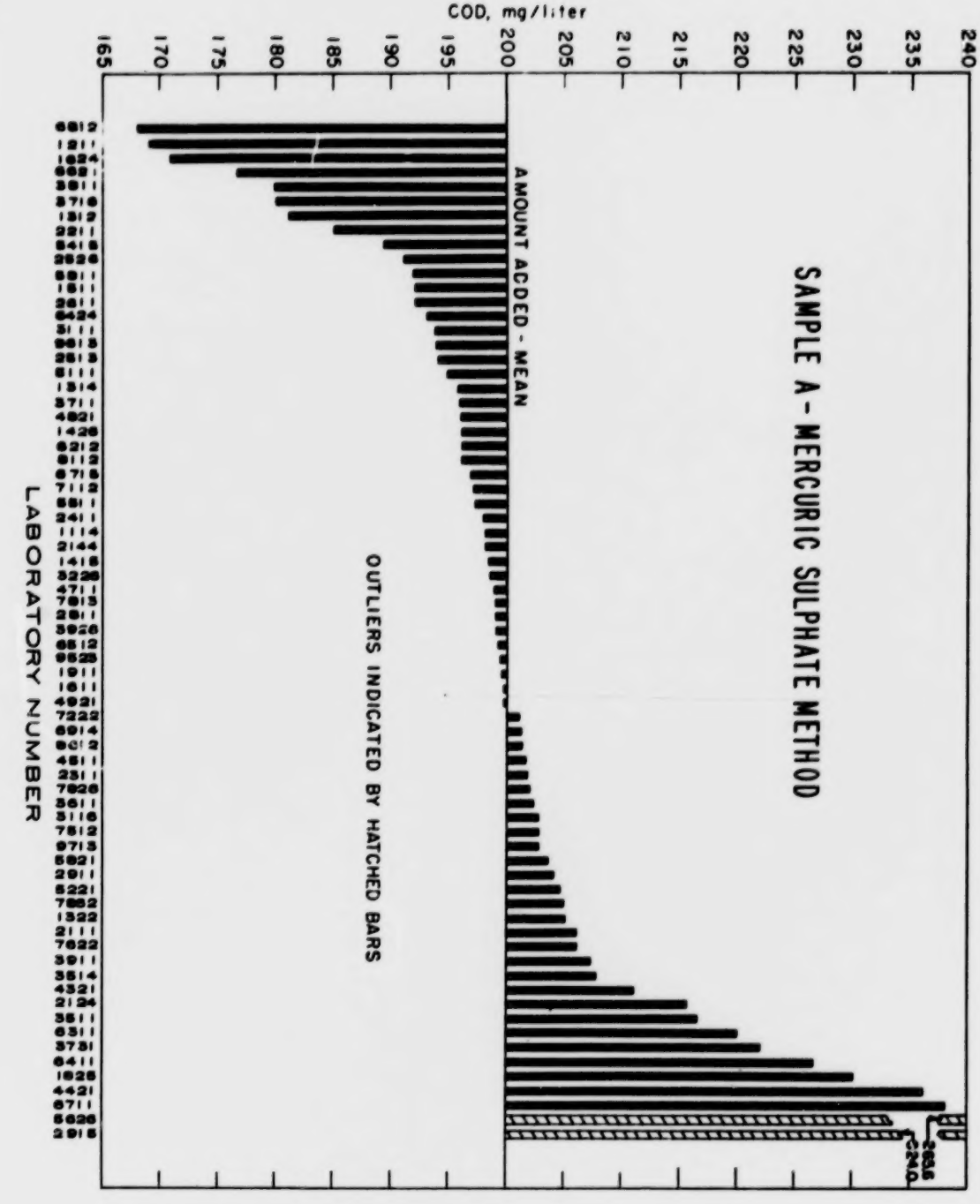
PROBABILITY CURVE FOR SAMPLE A - STANDARD METHOD



PROBABILITY CURVE FOR SAMPLE A-MERCURIC SULPHATE


SAMPLE A - STANDARD METHOD
BLACK BARS DENOTE CHLORIDE CORRECTIONS (1), (1+2), (1+3)
AMOUNT ADDED
MEAN
COD, mg/liter
225
220
215
210
205
200
195
190
185
180
175
170
165
LABORATORY NUMBER

GPO 820-837-2


SAMPLE A - MERCURIC SULPHATE METHOD
COD, mg/liter
AMOUNT ADDED - MEAN
OUTLIERS INDICATED BY HATCHED BARS
LABORATORY NUMBER

SAMPLE B (160 mg/liter COD in distilled water containing 100 mg/liter chloride)

Sample B was designed to contain a moderate amount of interference, such as might be found in many surface waters. This amount of chloride would tend to produce a high COD result.

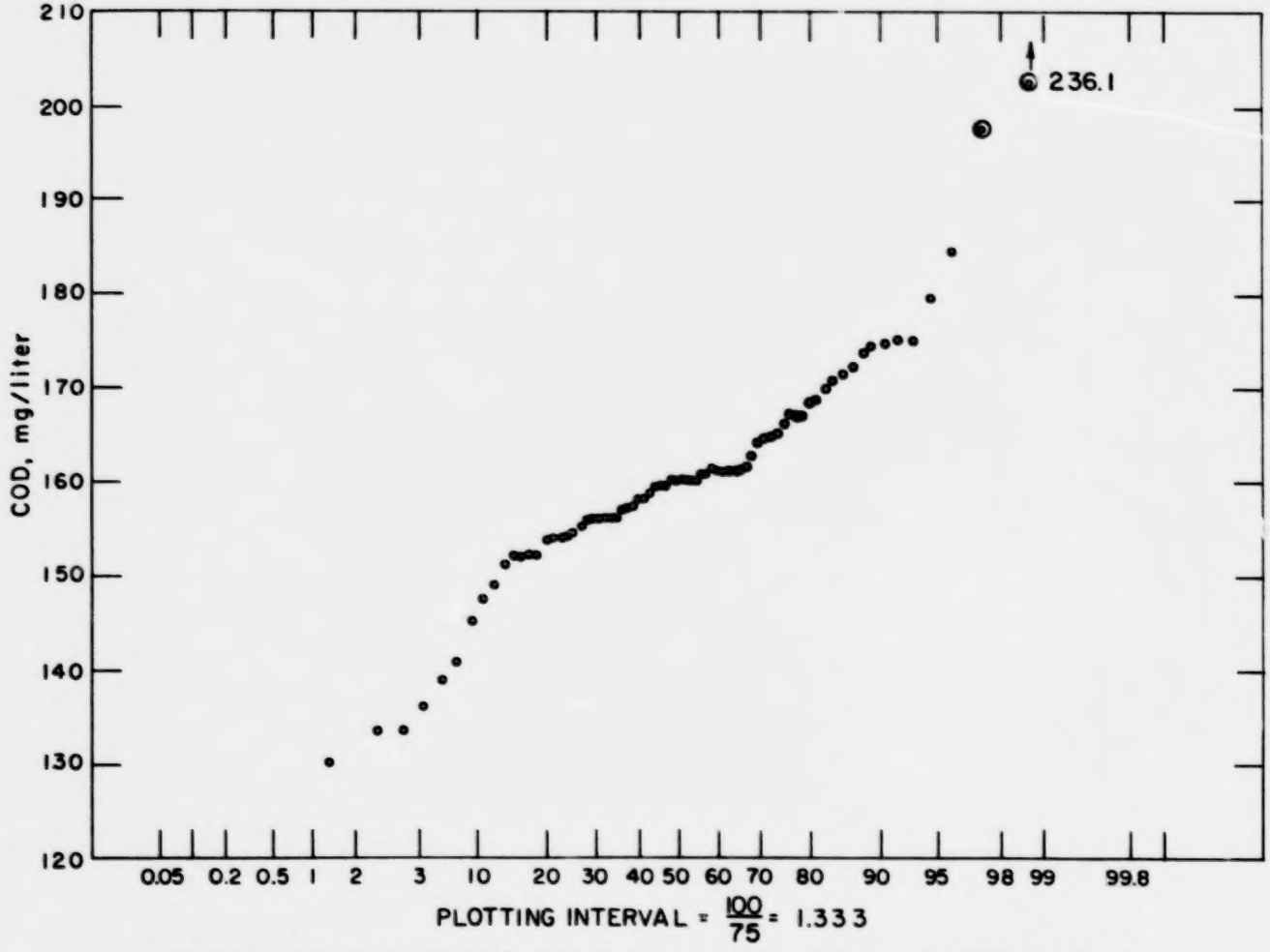
The mercuric sulfate method produced good accuracy as shown by the close agreement (Table 2) between the mean, median, and amount added. The 50% range shows that the better half of the results had an error of 5 mg/liter or less. Surprisingly, the precision as indicated by the standard deviation was a little better than on Sample A.

The standard method (overall) showed substantially less accuracy. The mean and median are in close agreement, but are about 8 mg/liter higher than the amount added. The 50% range of 11 mg/liter also indicates substantial inaccuracy in even the better half of the results. The results show a normal distribution and a precision nearly as good as on the control sample A.

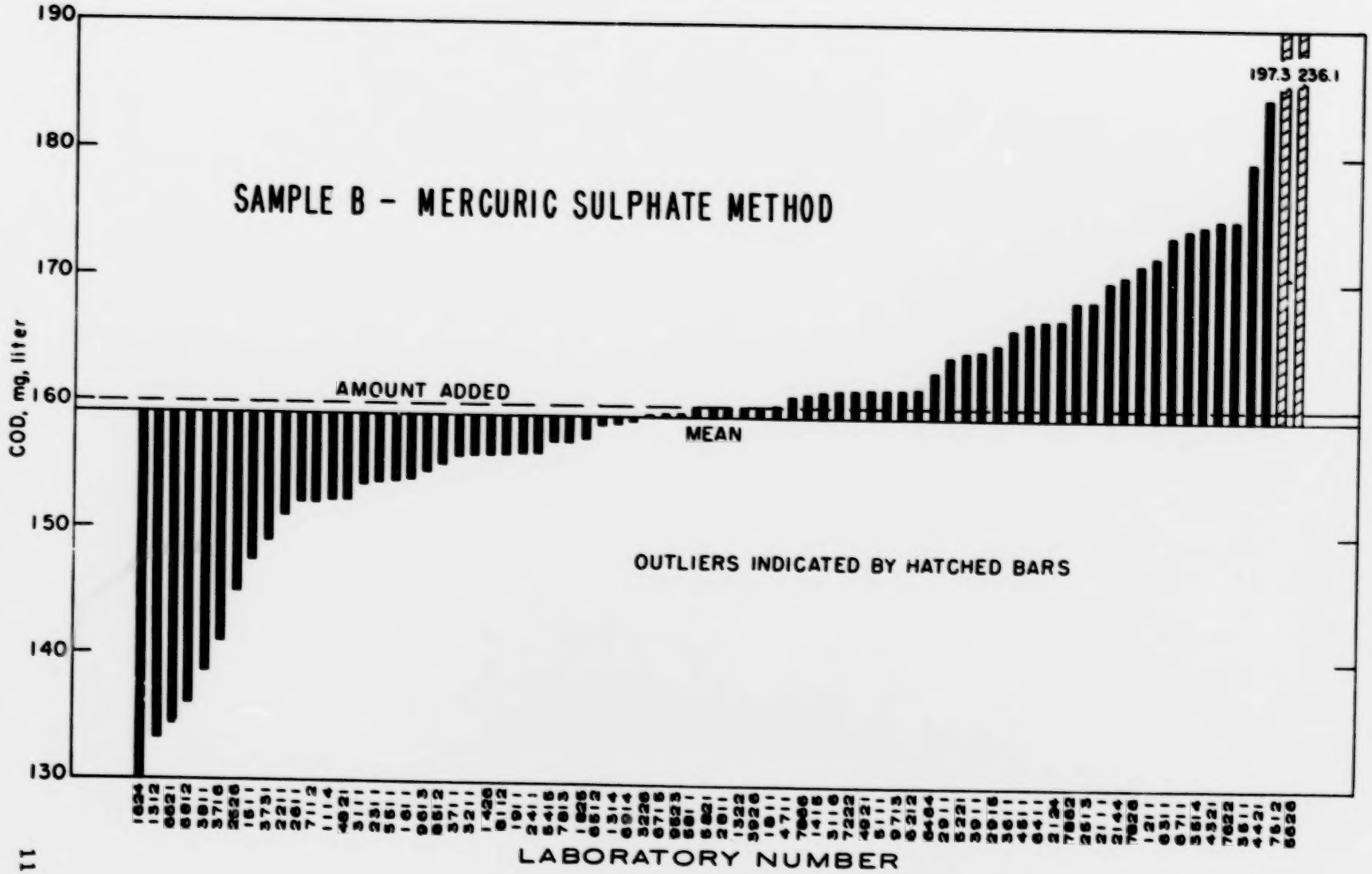
It is evident that on this type of sample substantially equal accuracy and precision can be obtained by use of either the mercuric sulfate method or the standard method when the mathematical correction is applied in conjunction with the procedure of refluxing for 20 minutes before adding silver sulfate (technique 1 and 3).

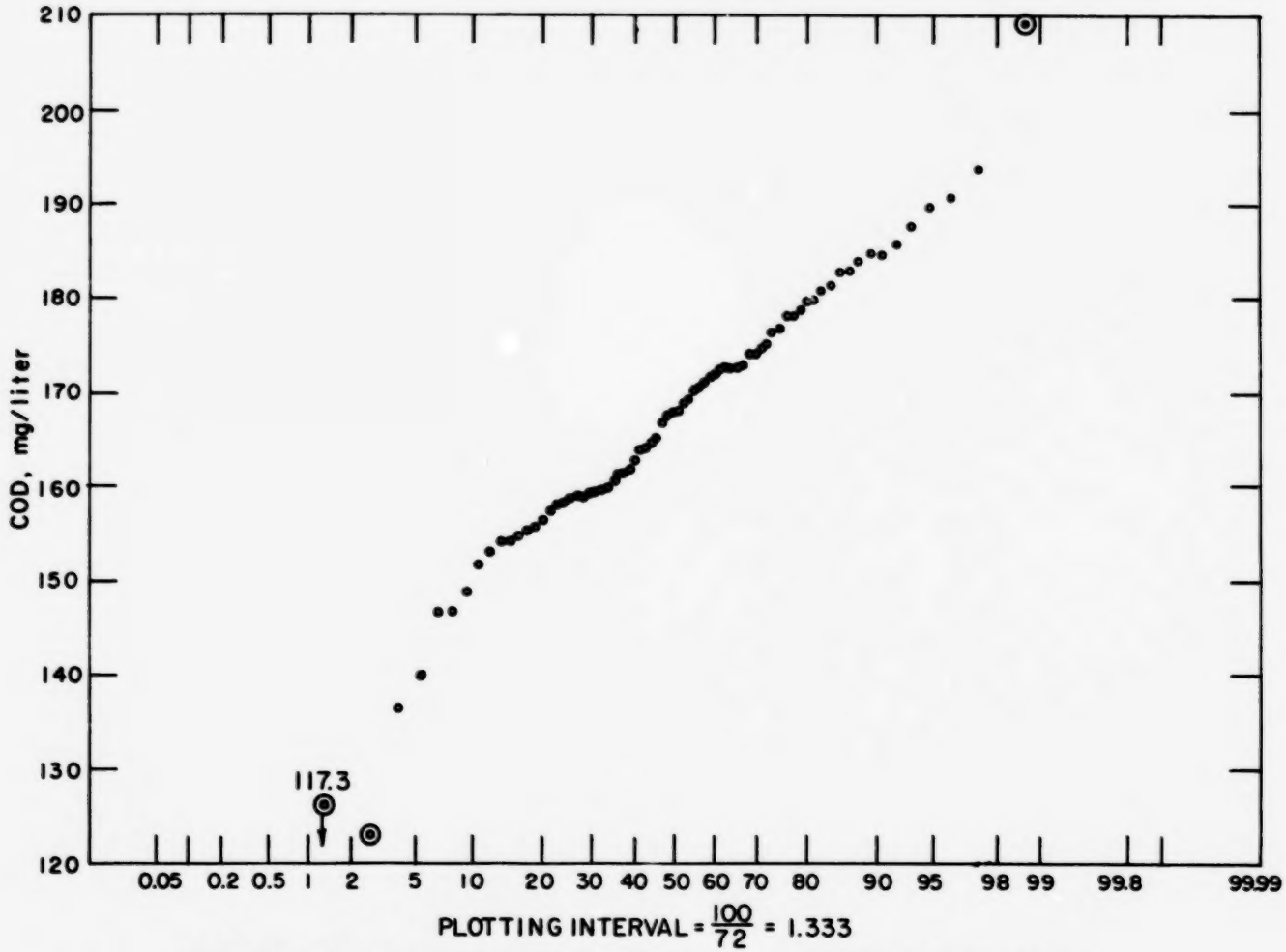
Table 2. SUMMARY OF STATISTICAL DATA ON SAMPLE B

Method	Mean	Standard deviation	Median	50% range	Number
Mercuric sulfate	159.1	10.4	159.9	± 5.0	72
Standard method, Overall	167.7	12.4	168.0	± 11.0	71
Standard method (1)	154.0	14.7	157.2	± 5.3	17
Standard method (2)	175.0	11.0	176.6	± 16.8	27
Standard method (3)	154.0	11.6	153.0	± 10.4	5
Standard method (4)	174.0	4.7	172.6	± 12.6	5
Standard method (1 + 2)	161.0	----	-----	------	2
Standard method (1 + 3)	159.0	11.8	159.3	± 1.4	9

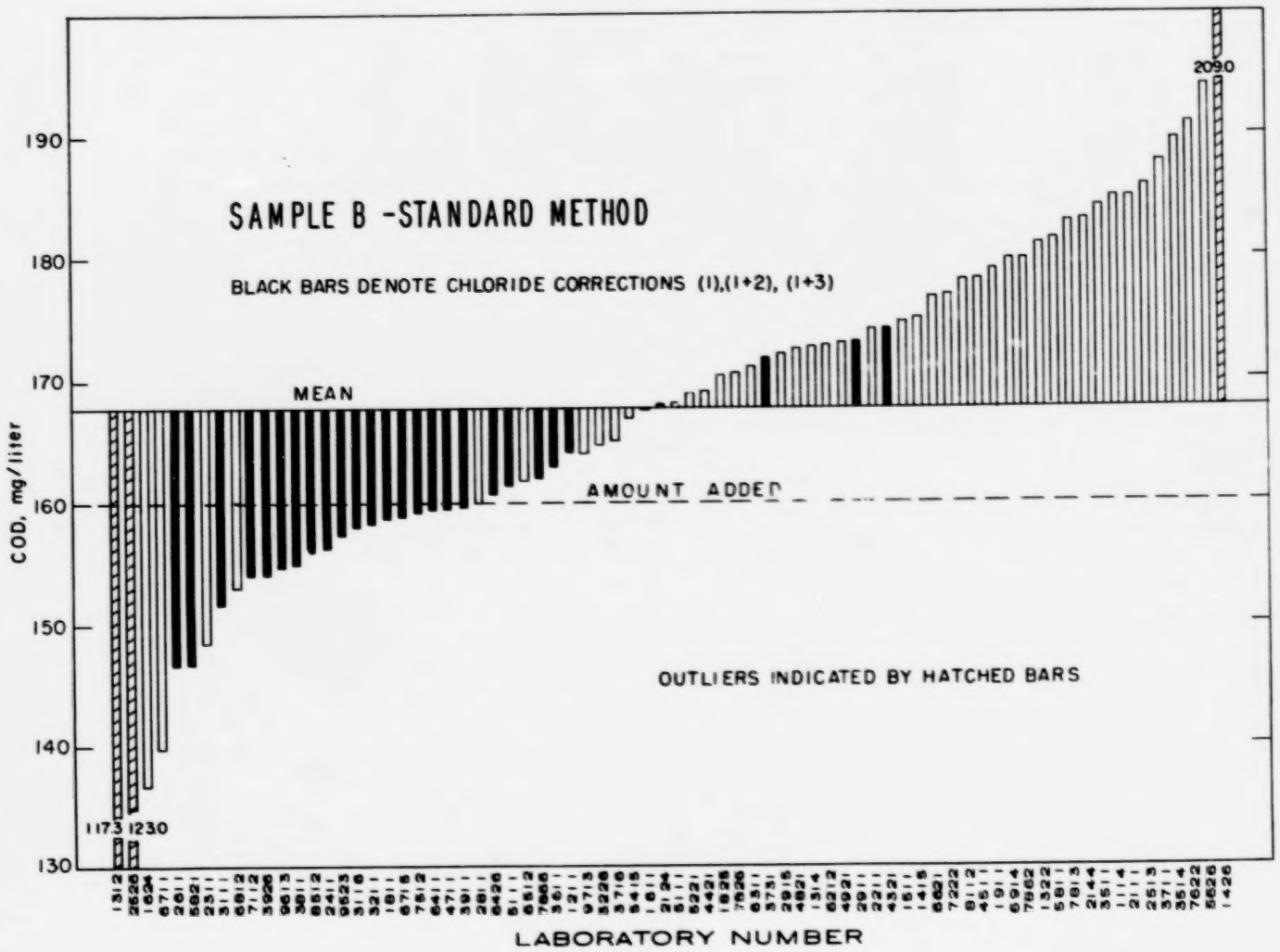


PROBABILITY CURVE FOR SAMPLE B - MERCURIC SULPHATE METHOD


SAMPLE B - MERCURIC SULPHATE METHOD
COD, mg. liter
190
180
170
160
150
140
130
AMOUNT ADDED
MEAN
197.3 236.1
OUTLIERS INDICATED BY HATCHED BARS
LABORATORY NUMBER



PROBABILITY CURVE FOR SAMPLE B - STANDARD METHOD


SAMPLE B -STANDARD METHOD
BLACK BARS DENOTE CHLORIDE CORRECTIONS (1),(1+2), (1+3)
MEAN
AMOUNT ADDED
OUTLIERS INDICATED BY HATCHED BARS
COD, mg/liter
LABORATORY NUMBER
190
180
170
160
150
140
130
2090
1173
1230

SAMPLE C (150 mg/liter COD in distilled water containing 1,000 mg/liter chloride)

The greatest difficulty with the COD test is experienced in analysis of waters of high chloride content, such as some rivers in the Southwest and estuary waters. Sample C was designed to represent a sample of this type.

The mercuric sulfate method produced results that were normally distributed and a precision that was nearly the same as on the control sample A. The values, however, showed a tendency to be slightly high (Table 3). The mean and median were in close agreement, but were approximately 6 mg/liter higher than the amount added; therefore, chloride oxidation may not have been completely inhibited in all cases.

The overall performance of the standard method was dramatically inferior. The general tendency was toward very high results with a mean value of 219.2 mg/liter and a median value of 200.8 mg/liter. The precision, as indicated by a standard deviation of 89.0, was poor.

Examination of the data showed that the results could be divided into two main groups. One group contained all values to which a mathematical correction for chloride interference had been applied - either combined with the use of silver sulfate added initially, added after 20 minutes of refluxing, or not used at all. The other group of values then included all results to which no mathematical correction had been applied, but which had involved the use of silver sulfate in some manner. Separate bar graphs show the results in these groups. One laboratory reported that no correction for chloride interference was used; therefore, this result appears only in the overall presentation. Statistical data showing further breakdown of the results into six separate groups according to the specific technique used for chloride correction appear in Table 3.

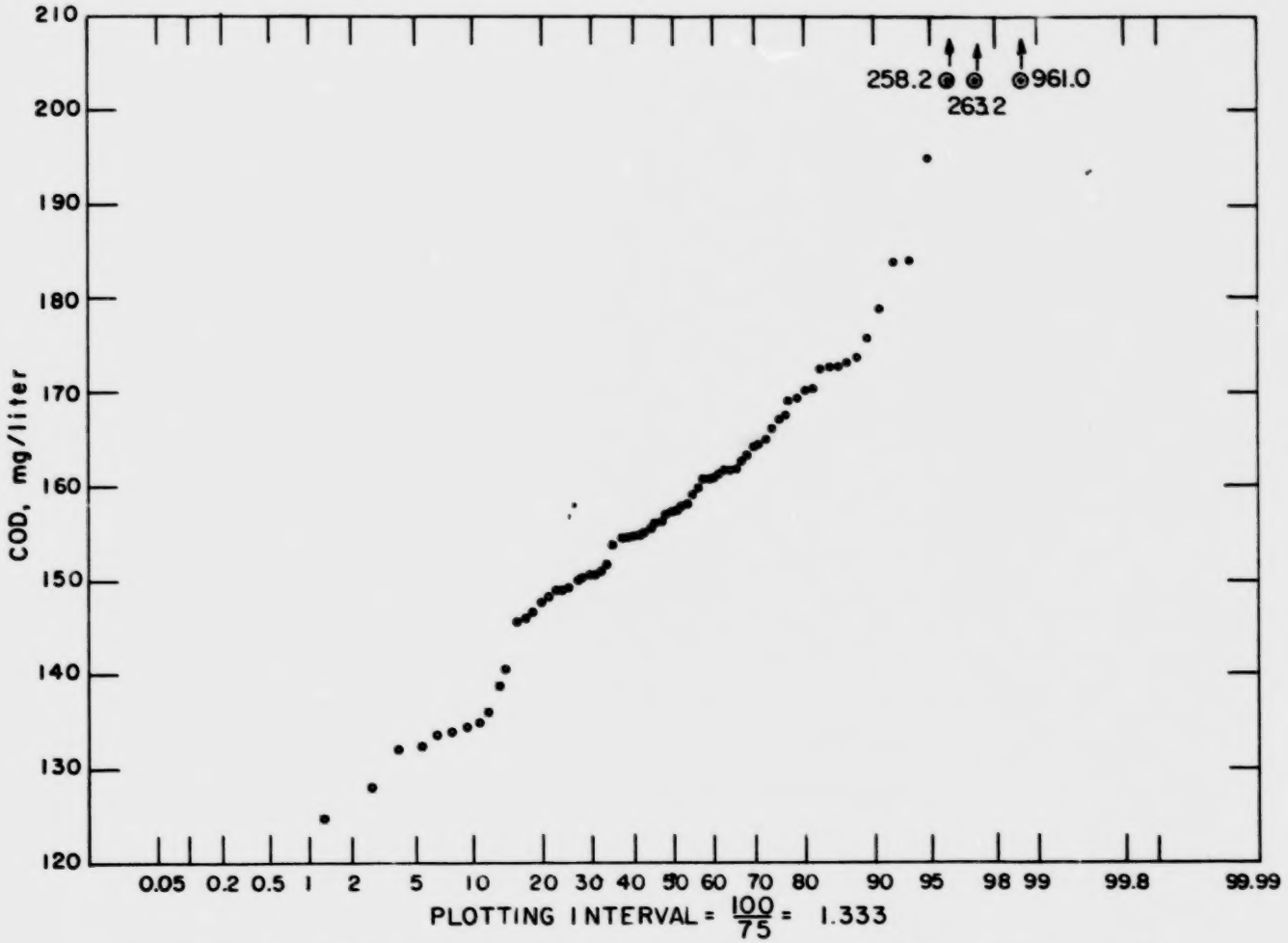
It is evident that, whether or not silver sulfate is used, a mathematical correction is mandatory for this level of chloride interference if the standard method is used. Although two laboratories reported adding silver sulfate initially, in conjunction with a mathematical correction (techniques 2 and 1), these two techniques are incompatible since the silver sulfate would produce a precipitate of silver chloride, which is only partially oxidized by the procedure, making the standard mathematical correction inapplicable. In spite of this, the results submitted by the two participants show much better accuracy than expected and are tabulated but unexplained.

Again, the technique that produced the best accuracy and precision for the standard method was the application of a mathematical correction in conjunction with 20 minutes refluxing before the addition of silver sulfate (techniques 1 and 3).

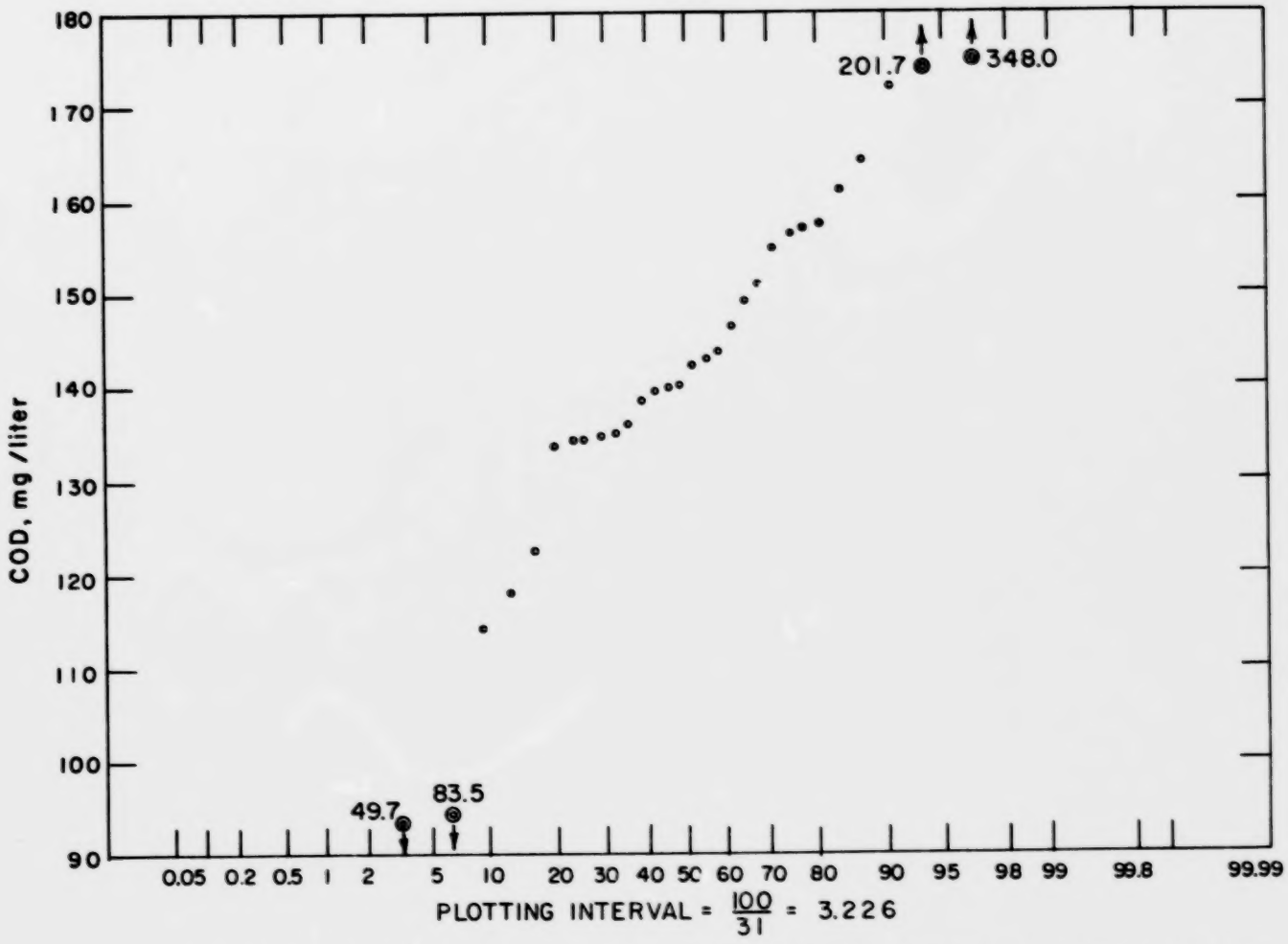
The use of silver sulfate as a catalyst was not necessary for any of the samples in this study. As a result, the participants that used only the mathematical correction achieved essentially the same accuracy as the group using both the mathematical correction and the silver sulfate after 20 minutes reflux. The latter technique, however, would have been required if the sample had contained materials such as straight-chain alcohols and acids that require the catalyst for complete oxidation.

Table 3. SUMMARY OF STATISTICAL DATA ON SAMPLE C

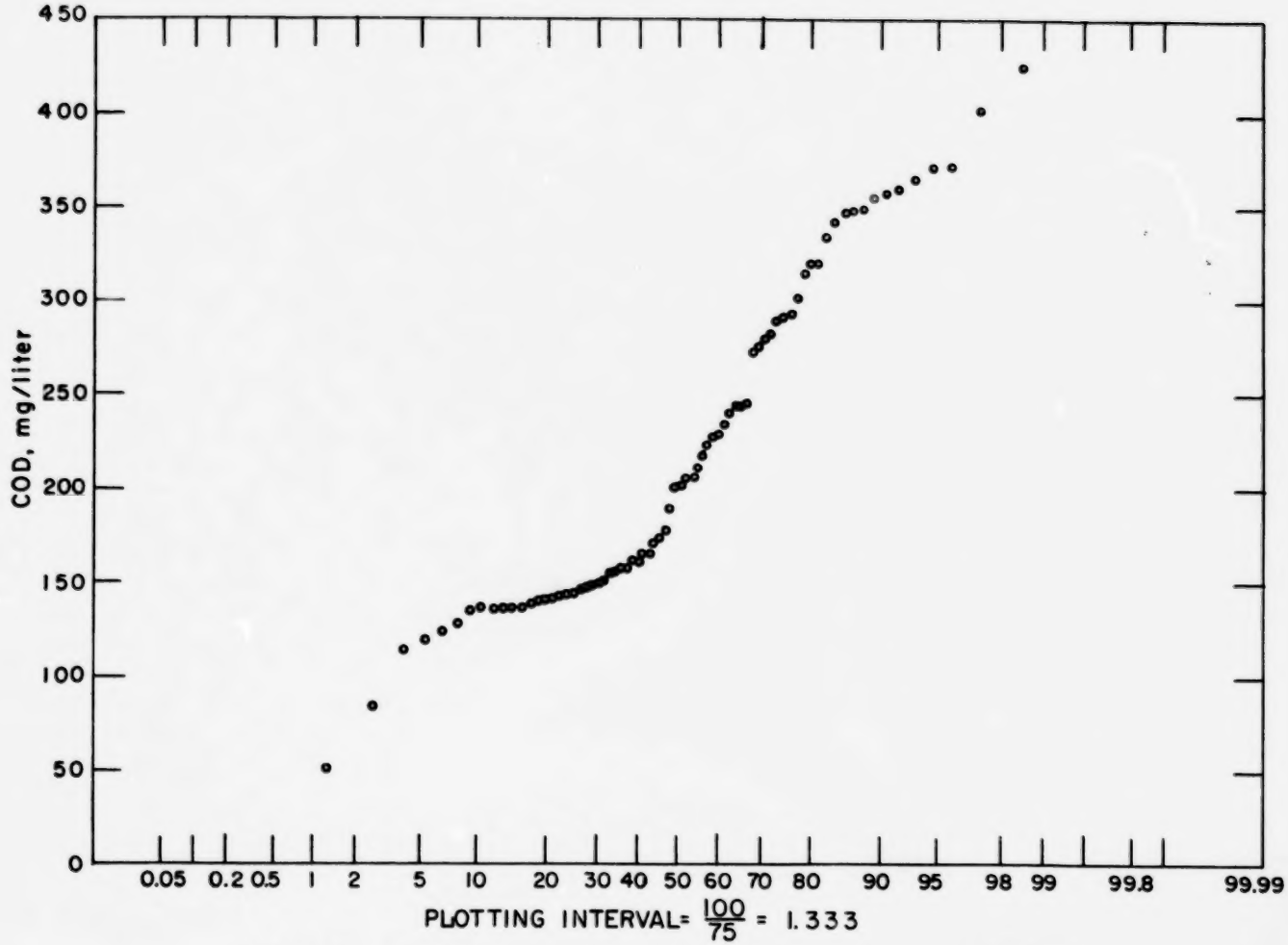
Method	Mean	Standard deviation	Median	50% range	Number
Mercuric sulfate	155.9	13.9	156.8	± 11.6	71
Standard method, Overall	219.2	89.0	200.8	± 55.3	74
Standard method (1)	147.6	58.0	143.4	± 11.8	18
Standard method (2)	282.8	66.0	285.8	± 132.3	30
Standard method (3)	221.6	112.9	147.9	± 23.0	5
Standard method (4)	233.8	75.5	224.9	± 61.0	8
Standard method (1 + 2)	138.7	-----	-----	------	2
Standard method (1 + 3)	146.6	22.6	139.8	± 10.2	10
Standard method (1) + (1 + 2) + (1 + 3)	143.0	13.8	141.2	± 10.3	26
Standard method (2) + (3) + (4)	266.6	76.2	270.9	± 120.9	43



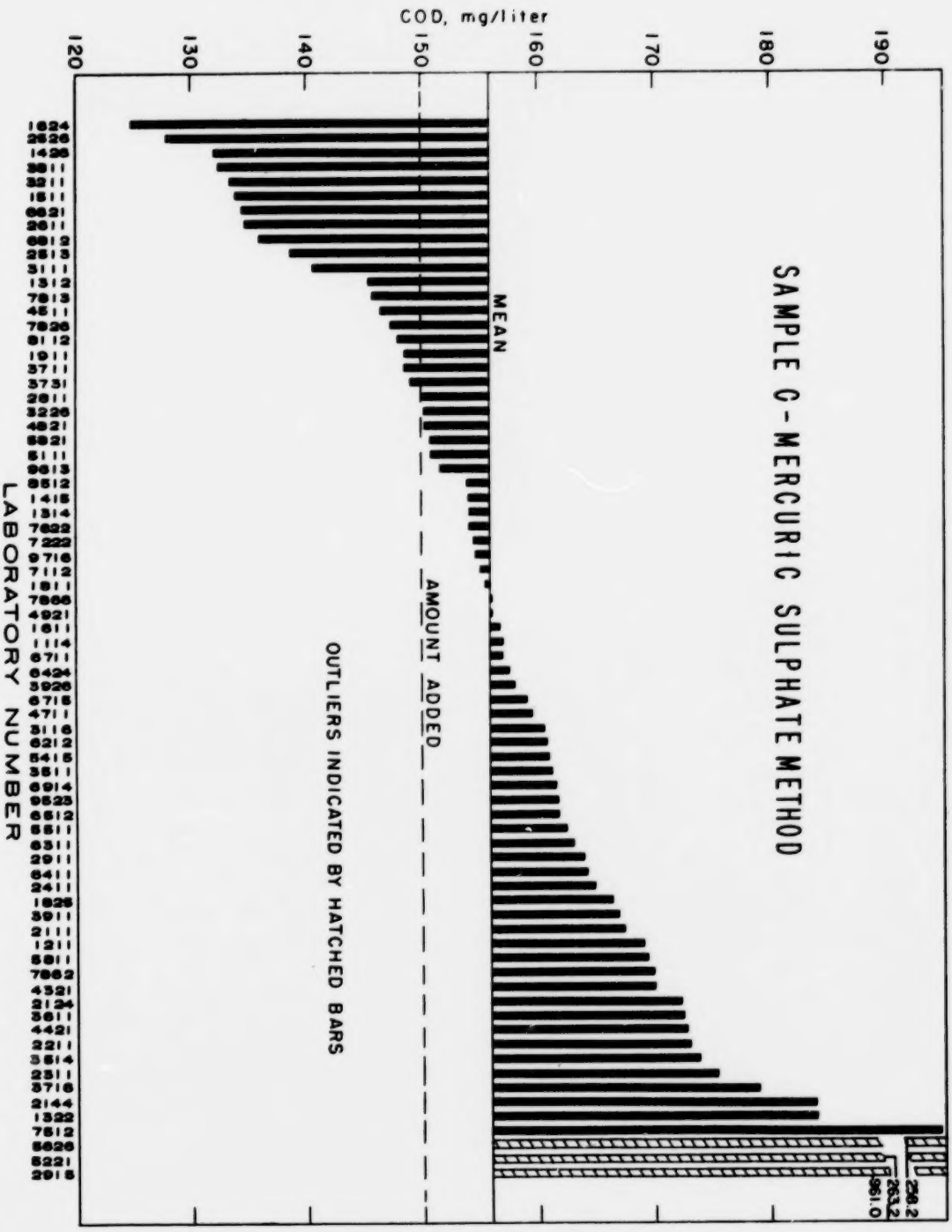
PROBABILITY CURVE FOR SAMPLE C- MERCURIC SULPHATE METHOD

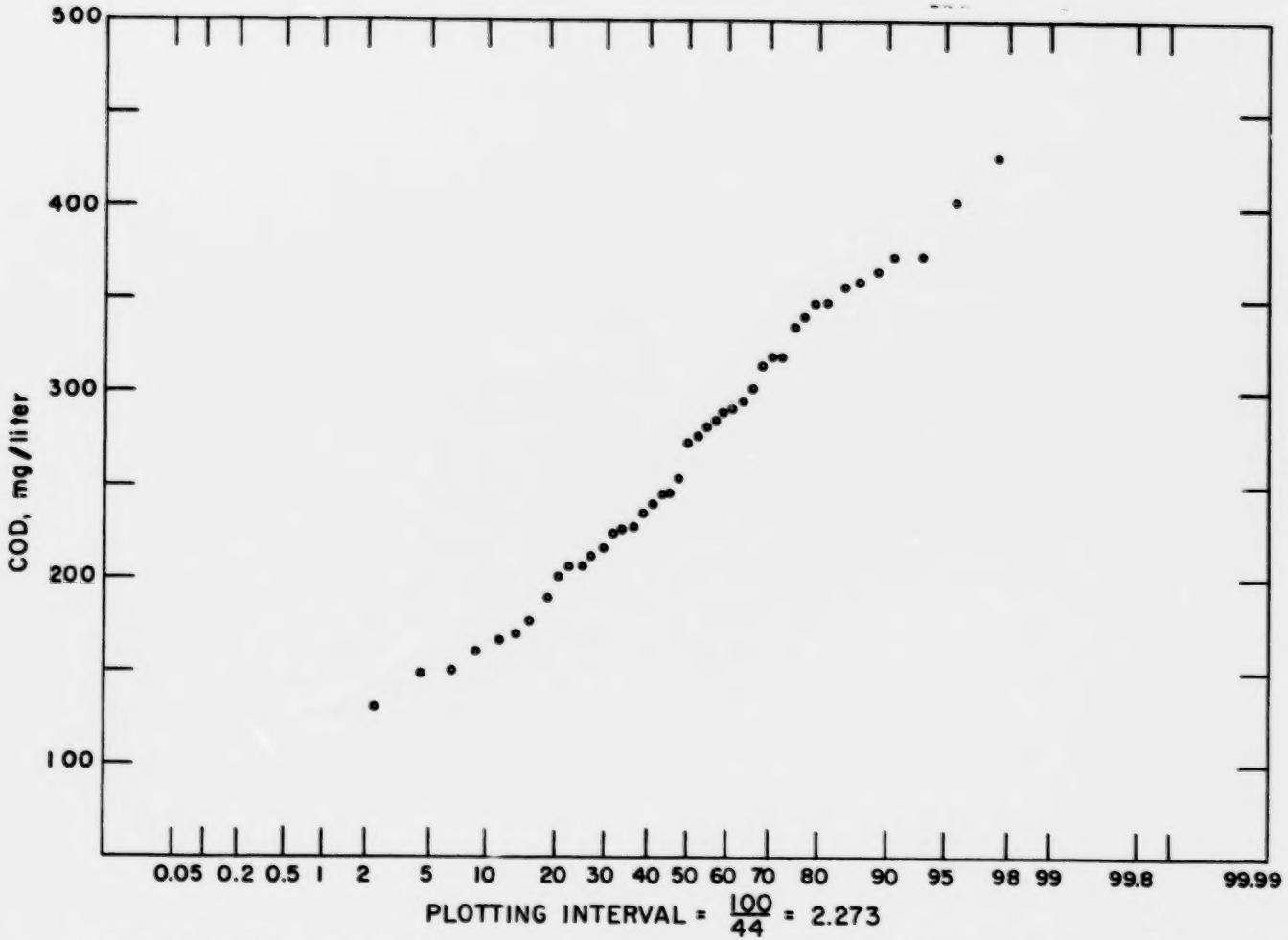


PROBABILITY CURVE FOR SAMPLE C-STANDARD METHOD, CHLORIDE CORRECTIONS (1), (1+2), (1+3)



PROBABILITY CURVE FOR SAMPLE C-STANDARD METHOD


SAMPLE C - MERCURIC SULPHATE METHOD
COD, mg/liter
120
130
140
150
160
170
180
190
MEAN
AMOUNT ADDED
OUTLIERS INDICATED BY HATCHED BARS
LABORATORY NUMBER
256.2
263.2
261.0



PROBABILITY CURVE FOR SAMPLE C-STANDARD METHOD, CHLORIDE CORRECTIONS (2), (3), (4)

SAMPLE C – STANDARD METHOD
CHLORIDE CORRECTIONS:
(1), (1+2), AND (1+3)
COD, mg/liter
110
120
130
140
150
160
170
180
AMOUNT ADDED
MEAN
OUTLIERS INDICATED BY HATCHED BARS
LABORATORY NUMBER
3611
5821
3611
1811
2611
7866
3911
5511
6411
7112
3211
9613
2526
6424
3926
2124
3111
8512
6715
1211
1312
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3116
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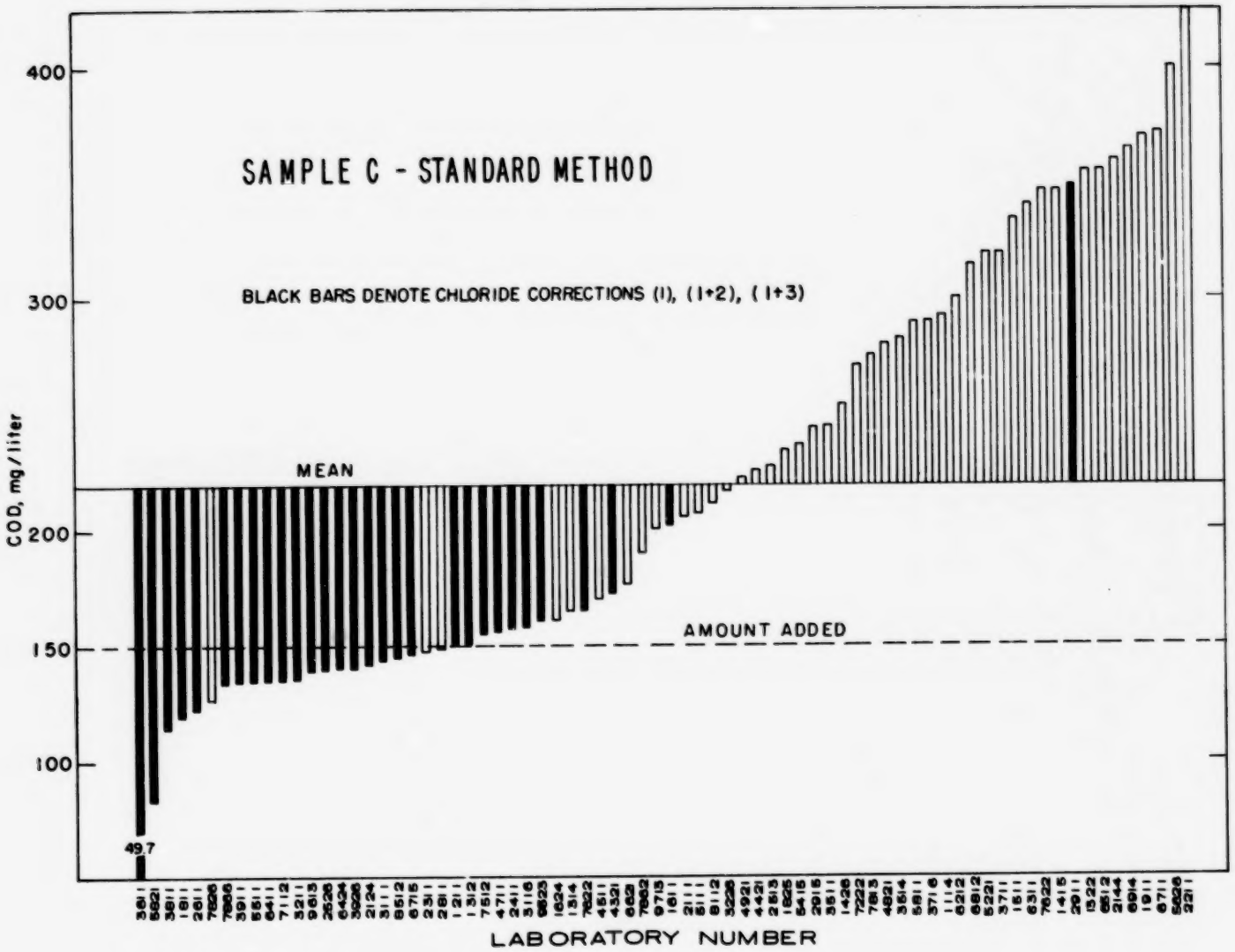
1611
2911
49.7
83.5
201.7
348.0


SAMPLE C - STANDARD METHOD
BLACK BARS DENOTE CHLORIDE CORRECTIONS (1), (1+2), (1+3)
MEAN
AMOUNT ADDED
COD, mg/liter
400
300
200
150
100
49.7
LABORATORY NUMBER

GPO 820-837-3

SAMPLE C - STANDARD METHOD
CHLORIDE CORRECTIONS:
(2), (3) AND (4)
COD, mg / liter
140
200
260
300
360
400
MEAN
AMOUNT ADDED
127.0
420
LABORATORY NUMBER
7826
2311
2811
9523
1314
4511
6621
7862
9713
2111
5111
8112
3226
4921
4421
2513
1825
5415
2915
3511
1426
7222
7813
4821
3514
5811
3716
1114
6212
6812
5221
3711
1511
6311
7622
1415
6512
2144
6914
1911
6711
5626
2211

SAMPLE D (40 mg/liter COD to be added to water sample collected by participant)

Sample D was designed to provide an overall estimate of the efficiency of the COD methods in analyzing a variety of collected samples (D_1) containing various amounts of chemically oxidizable material and interferences.

In preparing sample D_2, 5 ml of the sample D concentrate was made up to 500 ml by adding 495 ml of the collected sample (D_1). Since before analysis D_1 was not similarly diluted, sample D_1 contained 1% more of the collected sample than did D_2. That is to say, to make the samples strictly comparable, 495 ml of the collected sample should have been diluted with 5 ml of distilled water and this sample then called D_1.

To minimize confusion, additional manipulations, and possibly mathematical errors, it was decided to ignore the dilution factor in the instructions to participants. The submitted results were then corrected by the Analytical Reference Service staff to compensate for the dilution. This was done by adding 1 % of the COD value for sample D_1 to the difference obtained by subtracting the initial COD value of D_1 from the COD value of D_2. This, in effect, raised the difference value to the value that would have been obtained if there had been no dilution of D_1 in the preparation of D_2. The theoretical value for D_2-D_1 was therefore adjusted to 40.0 mg/liter COD in every case. Statistical calculations were thereby simplified, and presentation of the data in a manner comparable to that used in the other parts of this study was made possible.

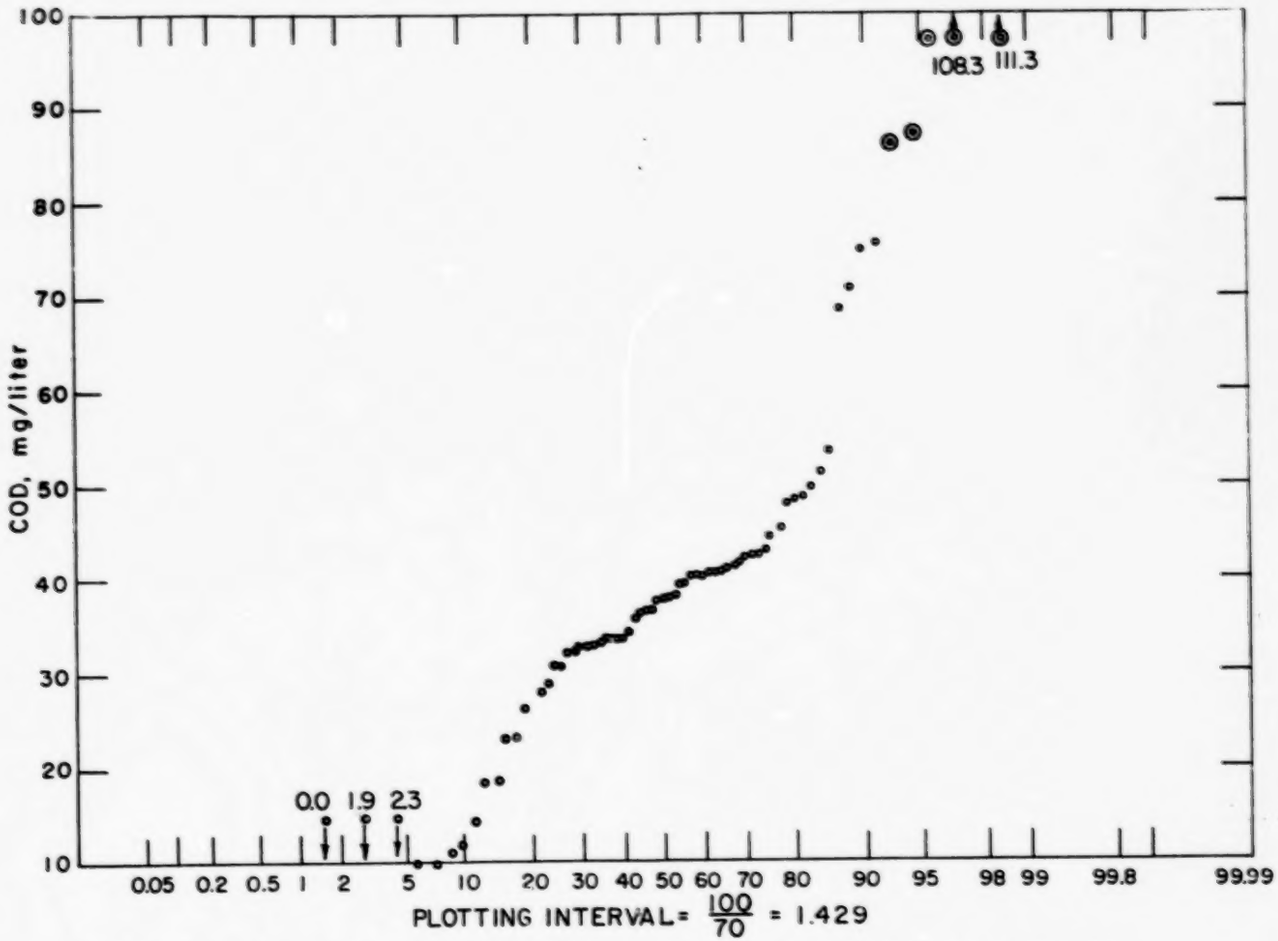
Since so many participants used a water having a very low COD for sample D_1, it is unfortunate that the instructions referred only to the high COD procedures, although many participants did use the low COD procedure. Without doubt, many results would have been improved by using the N/40 reagents rather than the N/4. In addition, the varied composition of the water used as sample D_1 precludes the use of statistical parameters in the usual manner, and they are, therefore, presented only for the purpose of aiding in the discussion of this sample and should not be used to predict the precision and accuracy of results that might be obtained from a different sample.

Many of the participants provided considerable analytical data on the water used for sample D_1. Unfortunately, no significant correlation was found between the quality of the water and the results obtained. Errors, such as neglecting to correct for high chlorides in the standard method, were self-canceling and did not affect the D_2-D_1 difference. Difficulties such as an endpoint obscured by color or turbidity undoubtedly caused inaccurate results, but were not reported in sufficient number to evaluate.

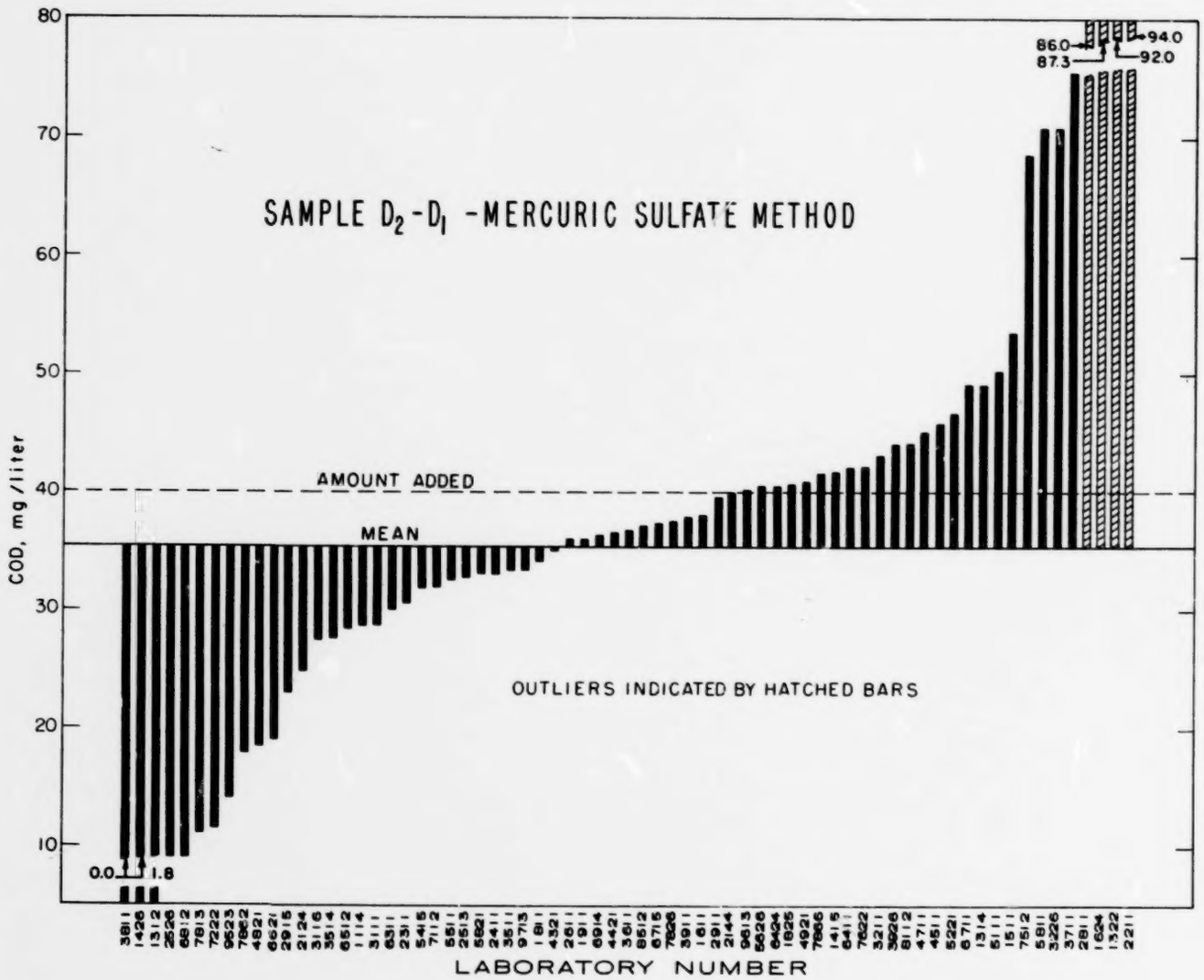
The data indicate (Table 4) that the mercuric sulfate procedure is slightlv more precise than the standard method, as shown by the standard deviationsof 15. 5 and 17. 0. The accuracy, however, was less, as shown by the deviation of the mean from the theoretical. On the other hand, the 50% range shows that the better half of the results and the median of all of the results obtained by either method are in close agreement. The differences are not considered significant, and it is the opinion of the Analytical Reference Service staff that either method would be suitable for most of the D_1 samples.

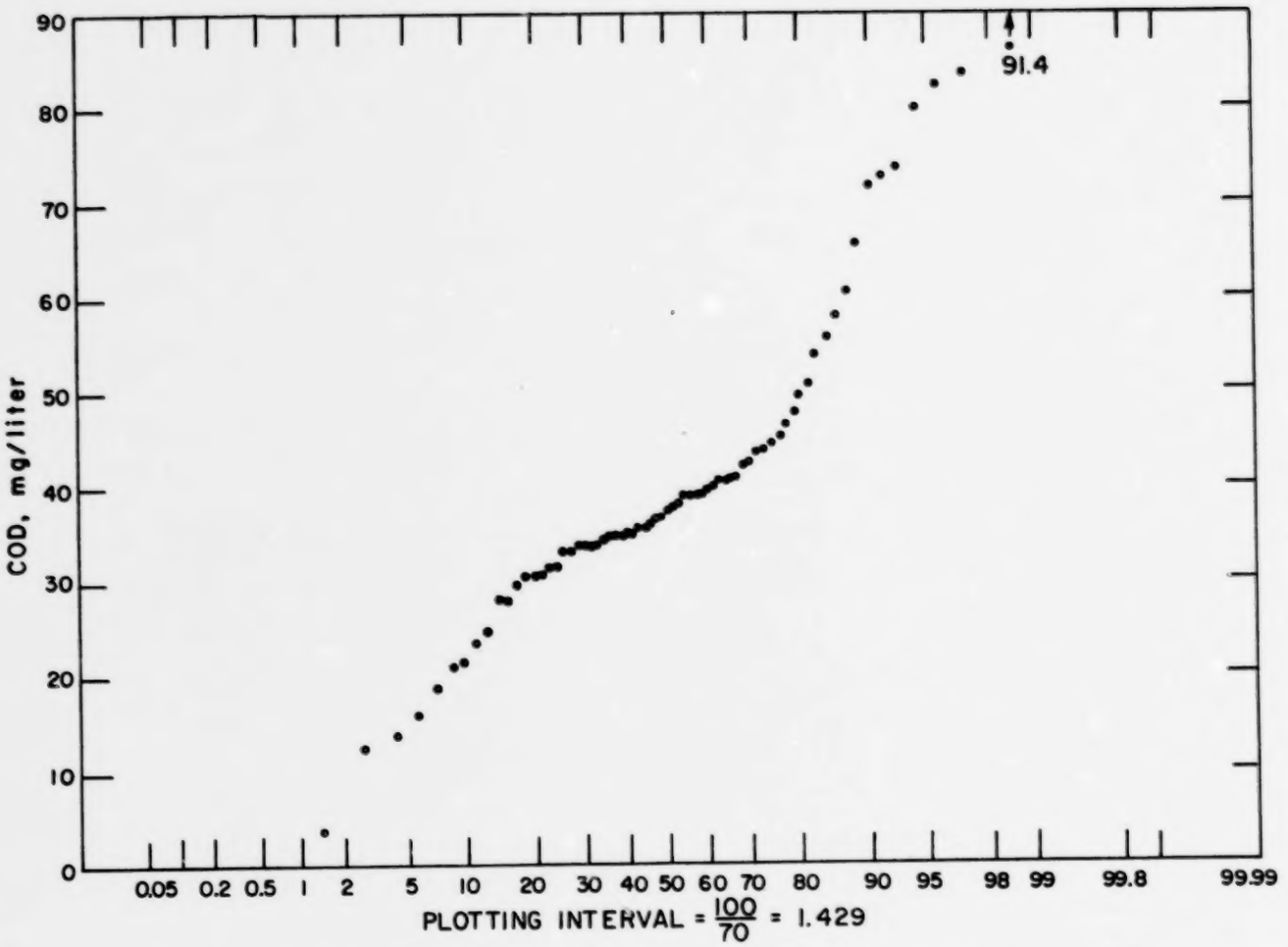
Table 4. SUMMARY OF STATISTICAL DATA ON SAMPLE D

Method	Mean	Standard deviation	Median	50% range	Number
Mercuric sulfate	35. 4	15. 5	36. 4	± 7. 4	64
Standard method Overall	40. 5	17. 0	37. 2	± 6. 9	69



PROBABILITY CURVE FOR SAMPLE D_2-D_1- MERCURIC SULPHATE METHOD


SAMPLE $D_2 - D_1$ -MERCURIC SULFATE METHOD
COD, mg/liter
80
70
60
50
40
30
20
10
AMOUNT ADDED
MEAN
OUTLIERS INDICATED BY HATCHED BARS
86.0
87.3
94.0
92.0
0.0
1.8
LABORATORY NUMBER



PROBABILITY CURVE FOR SAMPLE D_2-D_1 -STANDARD METHOD

COD, mg/liter
10
20
30
40
50
60
70
80
MEAN
AMOUNT ADDED
SAMPLE D_2-D_1 - STANDARD METHOD
LABORATORY NUMBER
3.9
.823
83.5
91.4
1312
6812
3514
5811
7826
2526
4821
3116
1624
6311
3711
7862
2411
5416
1426
1911
5626
3111
5511
7112
2144
4711
4421
6914
1114
7222
9613
8112
3811
4321
3611
1415
9525
7813
8512
6411
2124
8512
6621
3911
3511
2311
3926
6715
1811
2811
6711
1825
3211
2915
2911
6424
7866
7822
2811
5221
2513
5821
1611
1314
5111
9713
1511
4511
7512
3226
1322
4921
2211

COMMENTS OF PARTICIPANTS

The most frequent comment concerned the precipitate formed when mercuric sulfate was added to Sample C. A few participants found this troublesome in detecting the endpoint of the titration, but the majority experienced no difficulty. Several suggestions were made to use pumice stone or porcelain chips instead of glass beads to control bumping. The general opinion of the participants who used a mathematical correction for chloride in the standard method was that the mercuric sulfate method was quicker and just as good. Those who did not perform a chloride analysis found the weighing of mercuric sulfate a time-consuming extra step. Many suggestions were made to use more than the recommended 2-3 drops of indicator to improve the color change at the endpoint of the titration. Some participants took exception to the statement in the instructions for the mercuric sulfate method that the COD calculation was the same as that for the standard method.

In preparing the instructions it was assumed that since the mercuric sulfate method purports to eliminate chloride interference, it would be evident that the COD calculation would not include a correction factor for chloride.

It was suggested that quantitative control of excess mercuric sulfate might give better results for high chloride samples. This undoubtedly would be true for extremely saline waters which would require more than the specified 1 gram of mercuric sulfate to complex the chloride completely. This type of sample, however, would be a special case requiring further investigation.

A comment that the sample should be added last to the cooled acid-dichromate mixture to avoid loss of volatile fractions may have some virtue in special cases. This technique could then incorporate another suggestion that the mercuric sulfate be dissolved first in the sulfuric acid. A sample containing high chlorides and requiring the catalytic action of silver sulfate might not, however, be completely oxidized because of some of the silver sulfate precipitating with the chloride, if this technique were used.

SUMMARY AND CONCLUSIONS

The results from this study indicate that the two procedures produce similar precision and accuracy when no interfering materials are present. When high concentrations of chloride are present, the mercuric sulfate procedure will effectively remove the interference due to chloride oxidation. The standard method may produce equal precision and accuracy only if the proper technique is used; namely, the measurement of chloride concentration in order to be able to apply the mathematical correction (technique 1), and refluxing the sample with the acid-dichromate mixture for 20 minutes before adding silver sulfate if the catalyst is required (technique 3). Many inaccurate COD values are entirely due to inaccurate chloride analysis.

An alarmingly large number of participants were apparently unaware of the effect of chloride in the measurement of COD by the standard method. This is evident from the many comments expressing concern over the great difference in COD values produced by the two methods in the analysis of Sample C.

Undoubtedly, much of the difficulty is due to a lack of clarity in the procedure as written in the 11th edition of Standard Methods. It is hoped that the forthcoming 12th edition will be improved in this respect.

The Analytical Reference Service staff members feel that the mercuric sulfate modification is the best method for COD measurement because it is less time-consuming than the correctly performed standard method and will provide at least equivalent precision and accuracy regardless of interferences present. Additional benefits, described by Dobbs and Williams,[2] but not evaluated in this study, are the elimination of inaccuracies due not only to the series of cyclic changes from chlorine to chloride through the formation of chloramines in wastewater containing chlorides and a high concentration of ammonia, organic amine, or nitrogenous matter, but also the reaction of chlorine, produced by the oxidation of chlorides, with organic matter in the sample. The latter can materially affect the COD.

A statistical summary of the results is presented in Table 5.

Table 5. STATISTICAL SUMMARY

	Sample A	Sample B	Sample C	Sample D
Mg/liter COD added	200	160	150	40
Mg/liter chloride added	0	100	1000	0
Mean				
Mercuric sulfate	200.2	159.1	155.9	35.4
Standard method, overall	197.5	167.7	219.2	40.5
Standard method (1) + (1 + 2) + (1 + 3)			143.0	
Standard method (2) + (3) + (4)			266.6	
Median				
Mercuric sulfate	198.9	159.9	156.8	36.4
Standard method, overall	198.2	168.0	200.8	37.2
Standard method (1) + (1 + 2) + (1 + 3)			141.2	
Standard method (2) + (3) + (4)			270.9	
Standard deviation				
Mercuric sulfate	13.1	10.4	13.9	15.5
Standard method, overall	11.4	12.4	89.0	17.0
Standard method (1) + (1 + 2) + (1 + 3)			13.8	
Standard method (2) + (3) + (4)			76.2	
50% range				
Mercuric sulfate	± 4.6	± 5.0	± 11.6	± 7.4
Standard method, overall	± 4.8	±11.0	± 55.3	± 6.9
Standard method (1) + (1 + 2) + (1 + 3)			± 10.3	
Standard method (2) + (3) + (4)			± 120.9	

LITERATURE REFERENCES

1. Standard Methods for the Examination of Water and Wastewater 11th edition. APHA, AWWA, WPCF. New York, 1960.

2. Dobbs, R. A. and Williams, R. T. Eliminaticn of Chloride Interference in the Chemical Oxygen Demand Test. Anal. Che m. Vol. 35, p. 1064. 1963.

APPENDICES

APPENDIX A.

TABULATION OF RESULTS

Table A-1. SAMPLE A (Amount added = 200 mg/liter COD)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
1114	199.3 196.9 198.1	198.1	205.7 201.7 204.5	204.0	2
1211	177.0 138.0 193.0	169.0	200.0 207.0 200.0	202.0	1 and 3
1312		181.2		182.0	1
1314	196.4 194.4 196.4	195.7	200.0 200.0 196.0	198.7	4
1322	204.0 208.0 204.0	205.0	200.0 192.0 196.0	196.0	none made
1415		198.3		191.4	2
1426	204.0 196.0 188.0	196.0	228.0 224.0 224.0	225.0	4
1511	192.0 192.0 192.0	192.0	195.2 199.2 199.2	197.8	2
1611	195.8 195.8 207.4	199.7	170.0 172.8 170.0	170.9	1 and 3
1624	174.8 168.8 168.8	170.8	182.0 178.0 178.0	179.3	2
1911	201.5 197.5 199.5	199.5	189.0 191.0 192.9	191.0	2

Table A-1 SAMPLE A (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
2111	206.0 206.0 206.0	206.0	206.0 204.0 204.0	204.7	2
2124	217.1 214.7 215.1	215.6	208.0 203.2 208.0	206.4	1 and 2
2144	196.8 198.8 198.8	198.1	188.0 188.0 184.4	186.8	2
2211	185 185 184	185	247 214 207	223	2
2311	199.1 207.3 199.1	201.8	202.5 202.5 194.2	199.7	3
2411	198.8 196.1 198.8	197.9	198.0 191.4 199.2	196.2	1 and 3
2513	192.0 196.8 193.6	194.1	216.0 225.6 217.6	219.7	2
2526	189.4 198.3 185.0	190.9	183.1 177.0 167.2	175.8	1
2611	192.0 192.0 192.0	192.0	188.0 188.0 188.0	188.0	1
2811	200.5 198.4 197.8	198.9	200.5 198.6 194.7	197.9	3

Table A-1. SAMPLE A (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
2911	208 204 200	204	199 199 199	199	1
2915	832 816 824	824	188 196 188	191	4
3111	193.7 195.6 191.7	193.7	197.1 193.1 189.1	193.1	1
3116	202.3 202.3 203.5	202.7	204.9 203.9 204.5	204.4	1 and 3
3226	197.1 199.0 199.0	198.4	199.2 199.2 199.2	199.2	2
3511	217.6 217.6 214.4	216.5	222.4 217.6 222.4	220.8	2
3514	204.2 211.2	207.7	212.0 222.3	217.2	2
3611	204.8 201.1 201.1	202.3	211.4 204.1 204.1	206.5	1
3711	192.2 198.6 196.5	195.8	210.9 218.6 208.1	212.5	2
3716	181 181 179	180	179 179 181	180	2

Table A-1. SAMPLE A (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
3731	216.0 228.0 222.0	222.0	196.0 208.0 200.0	201.0	1
3811	172.6 182.7 178.4 185.8	179.9	204.0 200.0 208.9 202.7	203.9	1
3911	209.6 209.6 202.4	207.2	206.8 200.1 197.4	201.4	1 and 3
3926	197 196 205	199	195 195 190	193	1 and 3
4321	210 213 210	211	196 204 210	203	1
4421	237.1 246.2 225.1	236.1	180.2 189.3 175.0	181.5	2
4511	201.6 201.6 201.6	201.6	198.4 198.4 198.4	198.4	4
4711	198.8 196.8 200.7	198.8	195.2 197.2 193.2	195.2	1
4821	195.9 195.9 195.9	195.9	195.9 195.9 195.9	195.9	2

Table A-1. SAMPLE A (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
4921	199.7 199.7 199.7	199.7	199.7 199.7 199.7	199.7	2
5111	196.0 196.0 192.0	194.7	200.0 196.0 200.0	198.7	2
5221	206.6 204.6 202.6	204.6	186.6 186.6 186.6	186.6	2
5415	189.3 185.4 193.2	189.3	182.8 190.3 186.7	186.6	4
5511	197.2 197.2 197.2	197.2	201.1 207.1 205.1	204.4	1 and 3
5626		265.6		198.2	None
5811	194.9 190.2 190.2	191.8	199.5 194.9 194.9	196.1	2
5821	203.6 203.6 203.6	203.6	186.3 182.3 182.3	183.6	1
6212	192.0 200.0 196.0	196.0	182.0 186.0 192.0	186.6	2
6311	230.6 210.7 218.7	220.0	186.9 242.5 194.8	208.1	2

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Table A-1. SAMPLE A (continued)

Laboratory	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
6411	226.6 226.6 226.6	226.6	200.4 196.4 204.4	200.4	1 and 3
6424	194.3 192.4 192.4	193.0	192.7 188.7 192.7	191.4	1 and 3
6512	199.2 197.2 201.2	199.2	187.1 185.1 183.1	185.1	2
6621	169.0 184.3 176.6	176.6	207.4 207.4 207.4	207.4	2
6711	239.2 235.5 239.2	238.0	187.7 187.7 187.7	187.7	3
6715	197.0 197.0 196.0	196.7	199.4 199.4 197.4	198.7	1
6812	169 165 169	168	169 169 165	168	3
6914	199.2 203.2	201.2	198.0 194.0 198.0	196.7	2
7112	195 200 196	197	193 194 194	194	1 and 2
7222	205.2 199.1 199.1	201.1	199.1 201.2 199.1	198.8	2

Table A-1. SAMPLE A (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
7512	208.0 200.0 200.0	202.7	206.8 198.8 206.8	204.1	1
7622	208.8 204.6 204.6	206.0	204.6 200.4 204.6	203.2	2
7813	197.4 199.5 199.5	198.8	205.8 205.8 201.6	204.4	2
7826	202.0 202.0 202.0	202.0	196.8 ----- -----	196.8	3
7862	204.4 205.2 204.8	204.8	208.8 226.3 237.8	224.3	2 and 4
8112	192 200 196	196	199 199 203	200	4
8512	202.0 199.6 202.0	201.2	210.0 198.0 -----	204.0	1
9523	198.8 200.7 198.8	199.4	190.5 195.0 192.6	192.7	1
9613	192.4 193.9 195.1	193.8	195.1 194.7 196.2	195.3	1
9713	200.0 208.0 200.0	202.7	200.0 196.0 192.0	196.0	2
1825	226.4 211.7 222.3	230.1	190.1 191.4 191.4	191.0	2

Table A-2. SAMPLE B
(Amount added = 160 mg/liter COD + 100 mg/liter chloride)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
1114	151.4 154.2 151.0	152.2	187.2 184.0 182.8	184.7	2
1211	157 168 190	172	164 167 162	164	1 and 3
1312		133.2		117.3	1
1314	158.4 158.4 158.4	158.4	173.9 171.9 171.9	172.6	4
1322	160 160 160	160	180 180 184	181	none made
1415		161.1		174.9	2
1426	164 156 148	156	212 212 204	209	4
1511	147.4 147.4 147.4	147.4	175.5 179.3 169.2	174.6	2
1611	153.6 156.4 151.7	153.9	160.8 168.8 172.8	167.5	1 and 3
1624	130.8 130.8 128.8	130.1	142.0 146.0 122.0	136.7	2
1811	161.4 160.3 158.6	160.1	158.1 159.0 158.6	158.6	1 and 3

Table A-2. SAMPLE B (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
1911	153.6 158.4 156.4	156.1	176.9 178.8 180.8	178.8	2
2111	170.0 170.0 170.0	170.0	184.0 188.0 182.0	184.7	2
2124	169.7 163.7 167.7	167.0	166.7 166.7 170.3	167.9	1 and 2
2144	172.4 170.4 168.4	170.4	183.6 183.6 181.6	182.9	2
2211	148 157 148	151	174 172 175	174	2
2311	153.9 150.2 157.1	153.7	153.8 146.0 146.0	148.6	3
2411	156.6 155.1 156.6	156.1	154.2 157.0 157.3	156.2	1 and 3
2513	164.8 172.8 168.0	168.5	179.2 182.4 195.2	185.6	2
2526	144.3 150.2 140.6	145.0	114.8 127.4 126.7	123.0	1
2611	152.0 152.0 152.0	152.0	146.6 146.6 146.6	146.6	1

Table A-2. SAMPLE B (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
	160.2		160.3		
2811	160.5	159.9	160.0	159.8	3
	159.0		159.2		
	164		173		
2911	164	164	173	173	1
	164		173		
	166		172		
2915	168	165	172	172	4
	160		172		
	156.1		151.6		
3111	152.2	153.5	151.6	151.6	1
	152.2		151.6		
	161.2		157.5		
3116	161.2	161.2	158.3	158.0	1 and 3
	161.2		158.3		
	157.2		156.2		
3211	155.3	155.9	158.2	158.2	1
	155.3		160.2		
	158.0		173.7		
3226	158.0	159.3	160.0	164.6	2
	161.9		160.0		
	176.6		185.6		
3511	180.8	179.4	185.6	184.0	2
	180.8		180.8		
	174.6		189.5		
3514	180.5	174.5	185.3	189.4	2
	168.5		193.5		
	162.5		156.7		
3611	166.2	166.2	171.4	162.8	1
	169.9		160.4		

Table A-2. SAMPLE B (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
3711	156.3 155.1 155.9	155.8	187.1 190.6 185.3	187.7	2
3716	140 140 142	141	165 165 164	165	2
3731	165.0 171.0 112.0	149.0	153.7 161.7 199.7	171.7	1
3811	137.0 140.5 138.2	138.6	148.9 150.0 165.8	154.9	1
3911	165.2 166.8 161.6	164.5	161.6 158.0 158.8	159.5	1 and 3
3926	163 160 156	160	152 158 151	154	1 and 3
4321	174 178 174	175	171 171 181	174	1
4421	213.9 151.7 187.8	184.5	173.0 166.7 167.5	169.1	2
4511	173.4 165.3 161.3	166.7	182.2 182.2 170.0	178.1	4
4711	161.4 157.4 163.3	160.7	160.0 160.0 158.0	159.3	1

Table A-2. SAMPLE B (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
	152.2		176.4		
4821	152.2	152.2	172.3	172.3	2
	152.2		168.3		
	157.4		176.6		
4921	161.3	161.3	172.8	172.8	2
	165.1		169.0		
	164.0		168.0		
5111	164.0	161.3	168.0	168.0	2
	156.0		168.0		
	164.4		168.3		
5221	164.4	164.4	168.3	168.8	2
	164.4		169.3		
	158.3		164.3		
5415	154.5	157.0	171.7	166.8	4
	158.3		164.3		
	153.8		163.3		
5511	153.8	153.8	161.3	161.3	1 and 3
	153.8		159.3		
5626		236.1		193.8	None
	159.8		181.4		
5811	159.8	159.8	181.4	181.4	2
	159.8		181.4		
	163.9		146.6		
5821	159.9	159.9	146.6	146.6	1
	155.9		146.6		
	158.0		174.0		
6212	164.0	161.4	172.0	172.7	2
	162.0		172.0		

Table A-2. SAMPLE B (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
6311	174.9 171.0 174.9	173.6	174.9 167.0 171.0	171.0	2
6411	166.2 168.2 166.2	166.9	160.0 160.0 158.0	159.3	1 and 3
6424	164.8 162.8 160.8	162.8	162.6 158.6 160.6	160.6	1 and 3
6512	158.3 158.3 158.3	158.3	162.3 164.3 158.3	161.7	2
6621	142.1 126.7 134.4	134.4	176.6 176.6 176.6	176.6	2
6711	173.0 173.0 176.6	174.2	139.8 139.8 139.8	139.8	3
6715	159.3 159.3 159.3	159.3	159.3 157.5 159.3	158.7	1
6812	137 133 137	136	153 153 153	153	3
6914	161.4 157.4 157.4	158.7	178.4 180.3 180.3	179.7	2
7112	152 152 152	152	154 154 154	154	1 and 2

Table A-2. SAMPLE B (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
7222	166.6 156.5 160.5	161.2	180.8 178.8 170.7	176.8	2
7512	168.0 200.0 224.0	197.3	159.0 159.0 159.0	159.0	1
7622	167.0 179.0 179.0	175.0	185.0 196.6 190.9	190.8	2
7813	159.9 155.5 155.5	157.0	182.8 184.9 180.7	182.8	2
7826	171.3 171.3 171.3	171.3	165.2 177.2 169.2	170.5	3
7862	162.4 174.3 -----	168.4	178.6 177.0 183.4	179.7	2 and 4
7866	152.4 165.0 165.4	160.9	165.0 161.5 159.1	161.9	1
8112	152 160 156	156	177 177 180	178	4
8512	155.2 155.2 -----	155.2	159.8 151.8 -----	155.8	1
9523	159.4 159.4 159.4	159.4	152.1 159.9 159.5	157.2	1

Table A-2. SAMPLE B (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
9613	154.0 155.1 154.8	154.6	153.4 153.8 156.9	154.7	1
9713	172.0 152.0 160.0	161.3	168.0 168.0 156.0	164.0	2
1825	157.2 157.2 -----	157.2	167.9 172.7 -----	170.3	2

Table A-3. SAMPLE C (Amount added = 150 mg/liter COD + 1000 mg/liter chloride)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
1114	154.2 153.8 163.0	157.0	287.4 291.5 298.3	292.4	2
1211	182 168 166 160	169	169 147 141 138	149	1 and 3
1312		145.4		150.8	1
1314	156.1 154.1 152.2	154.1	164.0 164.0 164.0	164.0	4
1322	184 192 176	184	352 356 356	355	none made
1415		153.9		347.3	2
1426	128 140 128	132	252 256 252	253	4
1511	137.7 129.9 133.8	133.8	334.3 330.5 338.2	334.4	2
1611	163.2 157.4 149.8	156.8	195.0 203.0 207.0	201.7	1 and 3
1624	128.8 118.8 126.8	124.8	164.0 130.0 190.0	161.3	
1811	154.6 155.0 156.6	155.4	116.0 118.3 120.0	118.1	1 and 3

Table A-3. SAMPLE C (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
1911	144.0 149.9 151.8	148.6	373.7 367.7 369.7	370.4	2
2111	166.0 168.0 168.0	167.3	200.0 204.0 212.0	205.3	2
2124	170.9 177.3 168.5	172.2	143.7 143.7 139.7	142.4	1 and 2
2144	181.2 186.0 184.4	183.9	364.8 354.4 360.4	359.9	2
2211	185 167 167	173	423 426 426	425	2
2311	179.0 179.0 168.0	175.3	150.0 146.0 146.0	147.3	3
2411	164.4 164.4 165.6	164.8	156.9 156.9 156.9	156.9	1 and 3
2513	144.0 137.6 134.4	138.7	236.8 217.6 228.8	227.7	2
2526	137.6 121.8 124.3	127.9	139.7 141.2 138.2	139.7	1
2611	132.0 132.0 140.0	134.7	119.6 127.6 119.6	122.3	1

Table A-3. SAMPLE C (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
2811	149.8 150.6 149.8	150.1	144.7 149.7 149.3	147.9	3
2911	164 164 164	164	348 348 348	348	1
2915	960 964 960	961	228 256 244	243	4
3111	140.1 140.1 142.0	140.7	142.9 142.9 142.9	142.9	1
3116	159.7 160.9 160.9	160.5	158.6 156.5 156.5	157.2	1 and 3
3211	133.4 133.4 -----	133.4	135.5 137.5 135.5	136.2	1
3226	148.3 148.3 154.1	150.2	216.7 216.7 216.0	216.5	2
3511	158.4 164.8 160.0	161.1	244.8 244.8 241.6	243.7	2
3514	179.5 166.7 175.2	173.8	273.2 290.0 283.8	282.3	2
3611	173.6 173.6 169.9	172.4	49.1 49.1 50.9	49.7	1

Table A-3. SAMPLE C (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
3711	148.6 147.8 149.5	148.6	292.2 324.1 340.9	319.1	2
3716	179 179 179	179	290 290 290	290	2
3731	168.0 168.0 112.0	149.0	-----	-----	1
3811	143.2 133.9 122.4 129.8	132.3	130.1 104.2 108.3	114.2	1
3911	164.0 160.8 176.0	166.9	135.8 134.2 132.6	134.2	1 and 3
3926	161 159 155	158	142 138 140	140	1 and 3
4321	170 172 168	170	173 169 173	172	1
4421	166.2 177.8 174.2	172.7	225.1 225.9 227.2	226.1	2
4511	145.2 149.2 145.2	146.5	170.0 174.1 166.0	170.0	4
4711	159.4 161.4 157.4	159.4	136.9 175.9 -----	156.4	1

Table A-3. SAMPLE C (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
4821	150.2 156.2 144.2	150.2	352.2 277.3 210.5	280.0	2
4921	153.6 157.4 157.4	156.1	222.7 215.0 230.4	222.7	2
5111	152.0 152.0 148.0	150.7	208.0 208.0 204.0	206.7	2
5221	296.4 237.1 256.2	263.2	325.0 302.0 328.8	318.6	2
5415	158.3 158.3 166.2	160.9	235.2 242.5 238.8	238.8	4
5511	165.6 161.7 159.7	162.3	138.8 130.9 132.9	134.2	1 and 3
5626	261.8 257.4 255.3	258.2	401.3 401.3 401.3	401.3	4
5811	164.0 184.0 160.0	169.3	320.0 284.0 264.0	289.3	2
5821	152.0 148.0 152.0	150.7	86.2 78.2 86.2	83.5	1
6212	160.0 158.0 164.0	160.7	304.0 300.0 298.0	300.6	2
6311	163.0 163.0 163.0	163.0	345.9 330.0 345.9	340.6	2

Table A-3. SAMPLE C (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
6411	162.2 164.2 166.2	164.2	134.6 134.6 134.6	134.6	1 and 3
6424	158.9 158.9 154.9	157.6	141.8 137.8 139.8	139.8	1 and 3
6512	163.0 163.0 159.0	161.7	355.9 353.9 357.8	355.9	2
6621	142.1 126.7 134.4	134.4	169.0 184.3 176.6	176.6	2
6711	161.9 154.6 154.6	157.0	368.0 375.0 372.0	371.7	3
6715	155.3 160.7 161.1	159.0	145.9 147.7 145.9	146.5	1
6812	137 133 137	136	314 314 314	314	3
6914	159.4 163.3 161.4	161.4	366.5 362.6 364.6	364.6	2
7112	156 152 156	155	135 139 131	135	1 and 2
7222	158.5 152.4 152.4	154.4	286.5 266.2 260.1	270.9	2

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Table A-3. SAMPLE C (continued)

Laboratory number	Mercuric sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
7512	200.0 184.0 200.0	194.7	149.4 165.4 149.4	154.7	1
7622	150.2 154.1 158.1	154.1	341.8 335.9 363.6	347.1	2
7622				164.0	1
7813	145.0 145.0 147.1	145.7	272.9 260.3 291.8	275.0	2
7826	148.0 150.0 144.0	147.3	131.0 123.0 127.0	127.0	3
7862	168.3 147.3 193.7	169.8	----- 183.4 195.7	189.6	2 and 4
7866	154.0 157.1 157.1	156.1	135.4 131.9 133.4	133.6	1
8112	148 148 148	148	211 211 212	211	4
8512	153.6 154.0 -----	153.8	145.4 142.2 -----	143.8	1
9523	162.1 165.3 157.4	161.6	153.1 163.9 165.9	161.0	1
9613	150.1 151.3 153.2	151.5	138.2 136.7 139.8	138.2	1

Table A-3. SAMPLE C (continued)

Laboratory number	Mercuric Sulfate method		Standard method		Chloride correction method
	Results	Mean	Results	Mean	
9713	164.0 148.0 152.0	154.6	188.0 208.0 204.0	200.0	2
1825	175.9 157.2 165.7	166.3	233.8 225.2 242.8	233.9	2

Table A-4. SAMPLE D (Amount added = 40 mg/liter COD)

Laboratory number	Mercuric sulfate method				Standard method				Chloride correction method
	Mean D_1	Mean D_2	Diff.	Corrected Diff.	Mean D_1	Mean D_2	Diff.	Corrected Diff.	
1114	50.4	80.5	30.1	30.6	69.5	103.1	33.6	34.3	2
1312	54.4	56.2	1.8	2.3	45.7	49.2	3.5	3.9	1
1314	97.0	147.2	50.2	51.2	93.7	150.5	56.8	57.7	4
1322	627.0	729.0	102.0	108.3	633	709	76	82.3	none made
1415	12.1	54.1	42.0	42.1	10.5	46.4	35.9	36.0	2
1426	191	183	0	1.9	268	296	28	30.7	4
1511	6.4	74.7	68.3	68.4	9.2	80.8	71.6	71.7	2
1611	297.0	334.1	37.1	40.1	273.8	326.3	52.5	55.2	1 and 3
1624	518.8	610.8	92.0	97.2	568.7	587.3	18.6	24.3	2
1811	8.7	42.8	34.1	34.2	1.9	42.2	40.3	40.3	1 and 3
1911	14.0	50.3	36.3	36.4	67.5	98.0	30.5	31.2	2
2124	123.4	148.3	24.9	26.1	124.9	161.4	36.5	37.7	1 and 2
2144	6.3	46.7	40.4	40.5	2.3	35.9	33.6	33.6	2
2211	129	239	110	111.3	145	235	90	91.4	2
2311	6.7	38.7	32.0	32.1	1.2	40.6	39.4	39.4	3
2411	477.5	506.2	28.7	33.5	491.3	516.7	25.4	30.3	1 and 3
2513	9.1	42.1	33.0	33.1	28.8	78.9	50.1	50.4	2
2526	73.1	82.0	8.9	9.6	40.2	60.8	20.6	21.0	1

Table A-4. SAMPLE D (continued)

Laboratory number	Mercuric sulfate method				Standard method				Chloride correction method
	Mean D_1	Mean D_2	Diff.	Corrected Diff.	Mean D_1	Mean D_2	Diff.	Corrected Diff.	
4511	239.2	284.9	45.7	48.1	199.7	269.9	70.2	72.2	4
4711	31.5	79.1	47.6	47.9	36.5	69.7	33.2	33.8	1
4821	0.0	18.4	18.4	18.4	7.5	28.6	21.1	21.2	2
4921	126.0	166.2	40.2	41.5	841.5	916.6	75.1	83.5	2
5111	16.0	69.3	53.3	53.5	25.3	85.3	60.0	60.3	2
5221	8.9	57.4	48.5	48.6	3.8	53.5	49.7	49.7	2
5415	427.7	456.0	28.3	32.6	436.8	462.7	25.9	30.3	4
5511	34.3	67.0	32.7	33.0	30.7	63.5	32.8	33.1	1 and 3
5626	112.8	152.4	39.6	40.7	66.1	96.9	30.8	31.5	none
5811	433.3	504.0	70.7	75.0	457.0	469.3	12.0	16.6	2
5821	28.9	62.0	33.1	33.4	8.1	61.7	53.6	53.7	1
6311	23.9	55.7	31.8	32.0	0	27.8	27.8	27.8	2
6411	58.9	100.5	41.6	42.2	60.3	97.1	36.8	37.4	1 and 3
6424	13.7	54.5	40.8	40.9	9.0	53.1	44.1	44.2	1 and 3
6512	16.5	45.2	28.7	28.9	30.9	67.8	36.9	37.2	2
6621	0.0	23.0	23.0	23.0	23.0	61.4	38.4	38.6	2
6711	27.0	76.1	49.1	49.4	18.4	58.9	40.5	40.7	3

Table A-4. SAMPLE D (continued)

Laboratory number	Mercuric sulfate method				Standard method				Chloride correction method
	Mean D_1	Mean D_2	Diff.	Corrected Diff.	Mean D_1	Mean D_2	Diff.	Corrected Diff.	
2611	45.3	81.3	36.0	36.4	38.6	78.6	40.0	40.4	1
2811	47.3	134.6	87.3	87.8	15.6	63.1	47.5	47.7	3
2911	36.0	76.0	40.0	40.4	17.0	60.0	43.0	43.2	1
2915	445.0	464.0	19.0	23.4	422.0	461.0	39.0	43.2	4
3111	11.3	41.8	30.5	30.6	8.0	40.9	32.9	33.0	1
3116	45.2	72.6	27.4	27.9	50.2	72.9	22.7	23.2	1 and 3
3211	0	43.0	43.0	43.0	0	42.3	42.3	42.3	1
3226	3.8	79.2	75.4	75.4	9.8	89.7	79.9	80.0	2
3511	16.3	49.6	33.3	33.5	20.3	59.2	38.9	39.1	2
3514	40.8	68.4	27.6	28.0	56.8	70.0	13.2	13.8	2
3611	104.8	141.5	36.7	37.7	77.1	111.9	34.8	35.6	1
3711	80.0	166.0	86.0	86.8	57.6	85.9	28.4	29.0	2
3811	0.0	0.0	0.0	0.0	17.6	52.1	34.5	34.7	1
3911	176.0	213.9	37.9	39.7	187.1	224.0	36.9	38.8	1 and 3
3926	50.0	94.0	44.0	44.5	56.0	95.0	39.0	39.6	1 and 3
4321	43.0	78.0	35.0	35.4	41.0	76.0	35.0	35.4	1
4421	18.8	56.1	37.3	37.5	1.6	35.4	33.8	33.8	2

Table A-4. SAMPLE D (continued)

Laboratory number	Mercuric sulfate method				Standard method				Chloride correction method
	Mean D_1	Mean D_2	Diff.	Corrected Diff.	Mean D_1	Mean D_2	Diff.	Corrected Diff.	
6715	7.3	45.3	38.0	38.1	6.6	46.8	40.2	40.3	1
6812	59.0	68.0	9.0	9.6	347.0	356.0	9.0	12.5	3
6914	4.0	40.5	36.5	36.5	7.8	41.8	34.0	34.1	2
7112	8.0	40.5	32.5	32.6	16.9	50.0	33.1	33.3	1 and 2
7222	32.5	44.0	11.5	11.8	59.6	93.5	33.9	34.5	2
7512	20.0	90.7	70.7	70.9	14.8	88.1	73.3	73.4	1
7622	22.4	64.5	42.1	42.3	21.1	67.2	46.1	46.3	2
7813	6.3	17.3	11.0	11.1	6.7	43.3	36.6	36.7	2
7826	354.4	390.4	36.0	39.5	367.4	382.6	15.2	18.9	3
7862	34.0	51.9	17.9	18.2	33.3	62.3	29.0	29.3	2 and 4
7866	16.9	58.6	41.7	41.9	19.8	64.7	44.9	45.1	1
8112	112.0	156.0	44.0	45.1	155.0	188.0	33.0	34.6	4
8512	24.5	62.0	37.5	37.7	14.7	53.2	38.5	38.6	1
9523	5.7	19.7	14.0	14.1	6.6	43.0	36.4	36.5	1
9613	8.4	48.8	40.4	40.5	9.4	43.8	34.4	34.5	1
9713	26.7	60.0	33.3	33.6	28.0	93.3	65.3	65.6	2
1825	0.9	41.6	40.7	40.7	16.0	57.5	41.5	41.7	2

APPENDIX B.

MERCURIC SULFATE PROCEDURE

A. Measure 50 ml of sample or aliquot diluted to 50 ml with distilled water, and place in a standard reflux flask, then add:

   (1) 1 gram mercuric sulfate

   (2) 5 ml concentrated H_2SO_4 - swirl to dissolve mercuric salt

   (3) 25 ml 0.25N $K_2Cr_2O_7$

   (4) 70 ml concentrated H_2SO_4 (cautiously)

   (5) 0.75 gram Ag_2SO_4

   (6) Several glass beads or porcelain chips

B. Mix well by swirling flask.

C. Connect flask to condenser and reflux for 2 hours.

D. Wash down the condenser with distilled water and cool to room temperature.

E. Add 10 drops of o-phenanthroline ferrous indicator, and titrate to a red endpoint with standardized ferrous ammonium sulfate (approx. 0.25N).

NOTE: Reagents, equipment, and calculations are the same as in Standard Methods.[1]

APPENDIX C.

GLOSSARY OF STATISTICAL TERMS

A glossary of statistical terms with definitions of their meaning as used in these reports is presented to insure uniform and complete understanding.

Arithmetic mean	The sum of a series of test results divided by the number in the series.
Median	The value above and below which an equal number of observations lie.
Accuracy	Accuracy is the correctness of a measurement, or the degree of correspondence between the result and the true value.
Accuracy Data	Measurements that relate to the difference between the average test results and the true result when the latter is known or assumed. The following measures apply: 50% Range - The maximum deviation from the true amount for the more accurate half of the mean results reported. Average deviation from true concentration - The average difference without regard to sign between each laboratory mean and the true value. Average percent deviation from established concentration (or amount added) - The average of the differences between a laboratory's replicate results and the established concentration expressed as percentages of the established concentration.
Precision	Precision is a measure of the reproducibility of measurements, or the degree to which the measurements correspond to one another.

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Precision Data

Measurements that relate to the variation among the test results themselves, i. e., the scatter or dispersion of a series of test results without assumption of any prior information. The following measures apply:

Variance - The sum of squares of deviations of the average test results from the mean of the series divided by one less than the total number of average test results.

Standard deviation - The square root of the variance.

Coefficient of variation - The standard deviation of the laboratories' means as a percentage of the mean of this series.

Range - The difference in magnitude between the highest and lowest laboratory mean.

Average percent deviation within laboratory - The average of the differences between a laboratory s replicate results and their mean, expressed as percentages of their mean.

Confidence limits - Limits within which the true mean of the series will lie with a given probability.

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APPENDIX D.

PROBABILITY EXPLANATION

This section deals with the description and use of normal probability paper. The bell-shaped normal distribution curve can be reduced to a straight line on probability paper. Obviously, it is easier to deal with this straight line than with the complicated bell-shaped curve.

Construction of Normal Probability Paper

In an ideal sample, frequencies of the measurements plotted against their magnitudes give a bell-shaped normal distribution curve. This curve is symmetric about its mean, 0, and the percentage of the area lying between any two points on the curve can be found. For example, 68.26% of the area under the curve lies between $\pm$ one standard deviation (Figure D-1).

The first step in the construction of normal probability paper is the transformation of the bell-shaped distribution curve to the probability summation curve. This curve gives the summation of the area from left to right under the bell-shaped curve up to any deviation. For example, taking the point, 0, on the X-axis of the summation curve, we read from the Y axis that 50% of the total area lies below this zero value, which is the mean. The summation of area up to a deviation of -1σ below the mean is $50 - 34.13$, or 15.87%, while the summation of area up to $+1\sigma$ above the mean is $50 + 34.13$, or 84.13%. Similarly, other transformations can be made to form a complete, smooth ogee or s-shaped curve (Figure D-2).

The next step is to reduce the probability summation curve to a straight line. This is done by projecting the points on the ogee curve vertically to the linear X-axis scale and by writing the corresponding percentage opposite each point. For example, project point a to a', and write its probability summation (15.87%); project b to b', and write 84.13%, etc. Such a scale, with the percentages shown, constitutes the X-axis of normal probability paper.

Plotting on Normal Probability Paper

Since the probability summation is the cumulative area from left to right, it represents probability of a measurement equal to or less than a given value. Arranging the data in ascending order

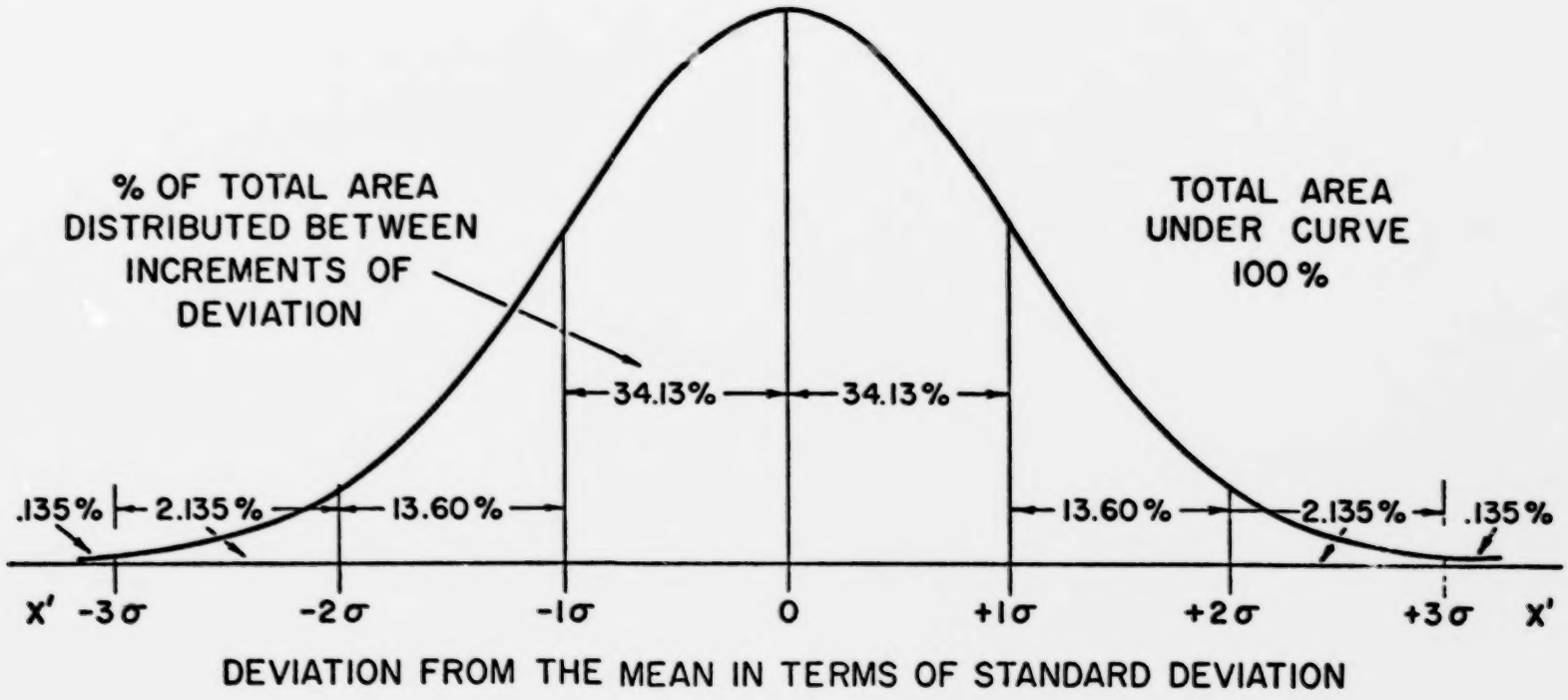

Figure D-1. The bell-shaped distribution curve.

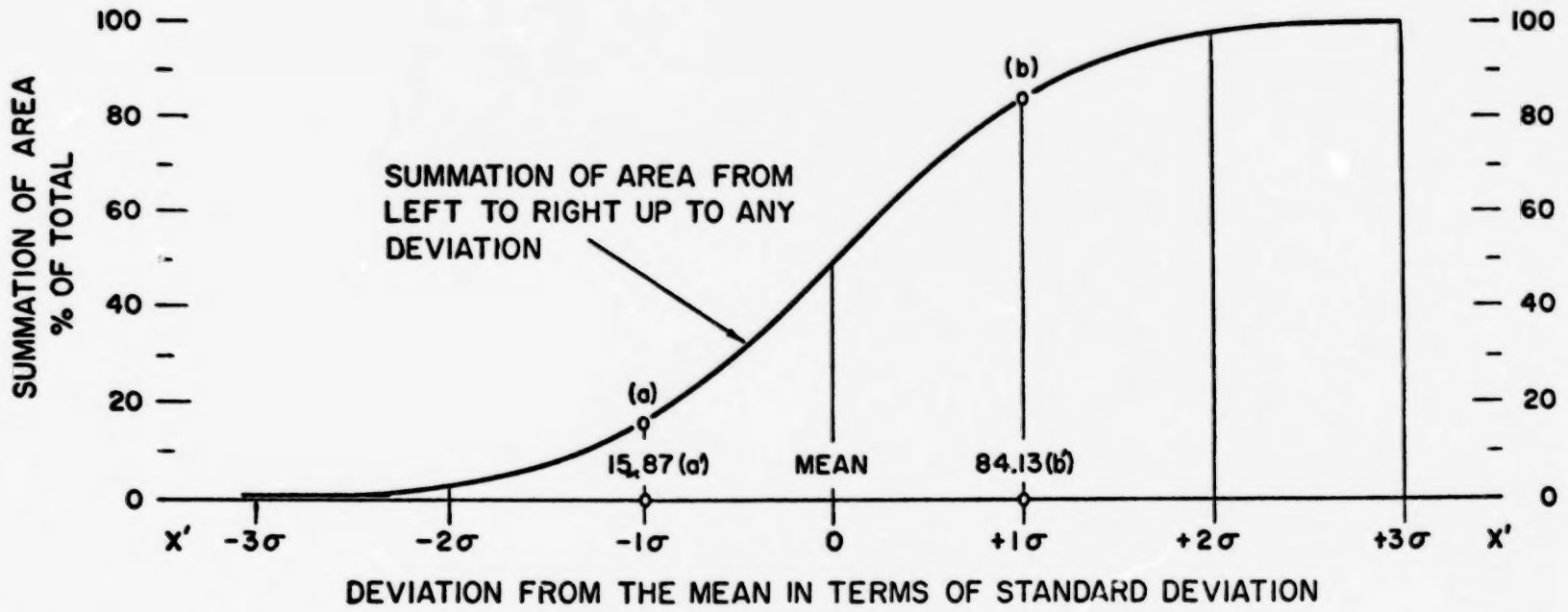

Figure D-2. The ogee summation curve.

of magnitude automatically places them in the order of their position on the probability summation scale. This arrangement permits ready determination of the probability not exceeding a certain magnitude of measurement.

In the development of the probability paper many difficulties were encountered in choosing a formula for plotting the position of the measurements on the probability summation scale (or X-axis), but the problem was solved in the following way. Ideally, the plotting position for the mean of any series, regardless of the number of values, is at 50 %; i.e., half of the values above and half below. If the mean is considered as part of the series, the number of plotting positions becomes n + 1. Thus the X-axis, which represents 100 %, is divided into n + 1 intervals. To plot the third point, for example, multiply $\frac{1}{n+1}$ by 3, or $3\left(\frac{1}{n+1}\right)$ The formula for the plotting interval, therefore, is $\frac{m}{n+1}$ where m equals the serial number of the measurements arranged in ascending order of magnitude, and n equals the total number of measured values to be plotted. Multiplication of the resulting value by 100 converts the ratio to a percentage.

In summary, the procedure for plotting data on normal probability paper is as follows:

1. Array data in order of ascending magnitude.

2. Calculate the plotting position of each value by the expression $\frac{m(100)}{n+1}$, which gives the ratio as a percentage. This point designates the percentage of the values that are equal to or less than the plotted value.

3. The Y-axis is graduated linearly from the lowest to the highest reported value, while the X-axis is graduated according to the probability scale. Place the first (lowest) value above the calculated plotting interval for m = 1 on the X-axis and at the appropriate value on the Y-axis. Plot the remaining values in a similar manner.

INTERPRETATION

If a straight line develops in the plotting, the data have a normal distribution; that is, in accordance with the theory of probability, this is the expected distribution of results.

If a straight line does not develop in the plotting, a change in the conditions affecting the observed measurements is suspected. It may mean, for example, that the same characteristic has not been measured under the same conditions.

Sometimes the great majority of the data approximate a straight line, but on the ends some results will be either extremely high or low. Just as one of these erratic results is far removed from the others on the bell-shaped normal curve, so it is far removed from the others on the straight-line curve. When this happens, these erratic results are presented in the published report on the probability curve, but the statistics are based on only the normal segment of the distribution.

REFERENCE

Velz, C. J. Graphical Approach to Statistics. Water and Sewage Works. pp. R106-R135. 1950

APPENDIX E.

ANALYTICAL REFERENCE SERVICE MEMBERSHIP

STATE AGENCIES

Alabama Water Improvement Commission
Arizona State Department of Health
Arkansas State Board of Health
California Department of Water Resources
California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
Colorado State Department of Public Health
Connecticut State Department of Health
Delaware Water Pollution Commission
Florida State Board of Health (Bureau of Laboratories, Jacksonville)
Florida State Board of Health (Division of Sanitary Engineering, Jacksonville)
Florida State Board of Health (Pensacola)
Florida State Board of Health (Winter Haven)
Hawaii State Department of Health
Idaho Department of Health
Illinois State Department of Public Health (Chicago)
Illinois State Department of Public Health (Springfield)
Illinois State Water Survey Division
Indiana State Board of Health
Kansas State Board of Health (Sanitary Engineering Laboratories)
Kentucky State Department of Health
Louisiana State Board of Health
Maryland State Department of Health
Maryland State Water Pollution Control Commission
Massachusetts Department of Public Health
Michigan State Department of Health
Michigan Water Resources Commission
Minnesota State Department of Health
Missouri Department of Public Health and Welfare
Montana State Board of Health
Nassau County Department of Health
Nebraska State Department of Health
Nevada State Department of Health (Las Vegas)
Nevada State Department of Health (Reno)
New Hampshire State Department of Health
New Hampshire Water Pollution Commission
New Jersey State Department of Health
New Mexico State Department of Public Health
New York State Conservation Department

North Carolina Department of Water Resources
New York State Department of Health
North Dakota State Department of Health
Ohio State Department of Health
Oklahoma State Department of Health
Oregon State Board of Health
Pennsylvania Department of Health
Puerto Rico Institute of Health Laboratories
Rhode Island Department of Health
South Carolina Water Pollution Control Authority
South Dakota Department of Health
Tennessee Division of Preventable Diseases
Tennessee Stream Pollution Control Board
Texas State Department of Health
Utah State Department of Health
Vermont State Department of Health
Vermont State Department of Water Resources
Virginia State Department of Health
Virginia State Water Control Board
Washington State Department of Health
West Virginia State Water Resources Commission
Wisconsin State Board of Health

MUNICIPAL AGENCIES

Air Pollution Control District, Pasadena, California
Alexander Orr Jr., Water Treatment Plant, Miami, Florida
City Department of Health, New York, New York
City Department of Public Health, Pasadena, California
City Department of Water, Dayton, Ohio
City Department of Water Resources, Durham, North Carolina
City Health Department, Baltimore, Maryland
City Health Department, Beaumont, Texas
City Health Department, Houston, Texas
City Water Department, Charlotte, North Carolina
Department of Air Pollution Control, Chicago, Illinois
Department of Public Works and Utilities, Flint Water Plant, Flint, Michigan
Department of Service and Buildings, Dayton, Ohio
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DHEW, PHS, Northeast Shellfish Sanitation Research Center, Narragansett, Rhode Island
DHEW, PHS, Off–Site Radiological Safety Program, Las Vegas, Nevada
DHEW, PHS, Water Quality Section, Division of Water Supply and Pollution Control, Cincinnati, Ohio
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Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee
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U. S. Department of the Interior, Geological Survey, Sacramento, California
Walter Reed Army Medical Center, Washington, D. C.

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Georgia Institute of Technology, Department of Applied Biology
Johns Hopkins University, School of Hygiene and Public Health
University of Kansas, School of Engineering and Architecture
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NALCO Chemical Company, Chicago, Illinois
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Reynolds Electrical and Engineering Company, Las Vegas, Nevada
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